

SOLUTIONS MANUAL

Elements of Chemical Reaction Engineering

THIRD EDITION

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Chapter 1

General: The goal of these problems are to reinforce the definitions and provide an understanding of the mole balances of the different types of reactors. It lays the foundation for step 1 of the algorithm in Chapter 4.

- P1-1.** This problem might encourage students to get in the habit of writing down what they learned from each chapter.
- P1-2.** Small open-ended question from which one could choose one or two parts. Parts (a), (b) or (e) are recommended.
- P1-3.** This problem use Example 1-3 to calculate a CSTR volume. It is straight forward and gives the student an idea of things to come in terms of sizing reactors in chapter 4. An alternative to **P1-11** and **P1-12**.

P1-4. Alternative to **P1-3**, **P1-11**, and **P1-12**. See **P1-3** above.

Problems **P1-5**, **P1-6**, and **P1-7** review the definitions given in the chapter.

- P1-8.** This problem can be assigned to just be read and not necessarily to be worked. It will give students a flavor of the top selling chemicals and top chemical companies.
- P1-9.** This problem will be useful when the table is completed and the students can refer back to it in later chapters. Answers to this problem can be found on Professor Susan Montgomery's equipment module on the CD-ROM. See **P1-17**.
- P1-10.** Many students like this straight forward problem because they see how CRE principles can be applied to an everyday example. It is often assigned as an in class problem and part (g) is usually omitted.

Problems **P1-11** and **P1-12** show a bit of things to come in terms of reactor sizing. Can be rotated from year to year with **P1-3** and **P1-4**. See **P1-3** above.

- P1-13.** Asks for details of operation of an industrial reactor.
- P1-14.** Encourages and requires the student to go outside the text for information related to CRE. May be a bit early in the text to assign this problem.
- P1-15.** Encourages and requires using other sources to obtain information.
- P1-16.** Encourages using other sources to obtain information.
- P1-17.** I strongly recommend this problem be assigned. It can be used in conjunction with Problem **P1-9**. Professor Susan Montgomery has done a

great job pulling together the material on real reactors in her equipment module on the CD-ROM.

P1-18. I always assign this problem so that the students will learn how to use POLYMATH/MatLab before needing it for chemical reaction engineering problems.

P1-19. As the WWW becomes more developed, it may be more and more important to assign this problem.

CDP1-A Similar to problems 3, 4, 11, and 12.

CDP1-B Points out difference in rate per unit liquid volume and rate per reactor volume.

Summary

	<u>Assigned</u>	<u>Alternates</u>	<u>Difficulty</u>	<u>Time</u>	<u>Solution Given</u>
P1-1	O				No
● P1-2(b)	AA	2(a),2(d), 2(e)	SF	15	c&d Yes
● P1-3	AA	3,4,11,12,A*	FSF	30	Yes
P1-4	AA	3,4,11,12,A	FSF	30	Yes
P1-5	I				Yes
P1-6	I				Yes
P1-7	I				Yes
● P1-8		- Read Only	SF	5	Yes
P1-9	O				Yes
P1-10	O		FSF	60	Yes
P1-11	AA	3,4,11,12,A	FSF	30	Yes
P1-12	AA	3,4,11,12,A	FSF	30	Yes
P1-13	I				Yes
P1-14	S/G				No
P1-15	S/G				Partial
P1-16	S/G				Partial
● P1-17			SF	45	No
● P1-18			SF	60	Yes
P1-19	I				No
CDP1-A	AA	3,4,11,12,A	FSF	30	
CDP1-B	I		FSF	30	

Assigned

● = Always assigned, AA = Always assign one from the group of alternates, O = Often, I = Infrequently, S = Seldom, G = Graduate level

Alternates

In problems that have a dot in conjunction with AA means that one of the problem, either the problem with a dot or any one of the alternates are always assigned.

Time

Approximate time in minutes it would take a B/B* student to solve the problem.

Difficulty

SF = Straight forward reinforcement of principles (plug and chug)

FSF = Fairly straight forward (requires some manipulation of equations or an intermediate calculation).

IC = Intermediate calculation required

M = More difficult

OE = Some parts open-ended.

*Note the letter problems are found on the CD-ROM. For example A \equiv CDP1-A.

Summary Table Ch-1

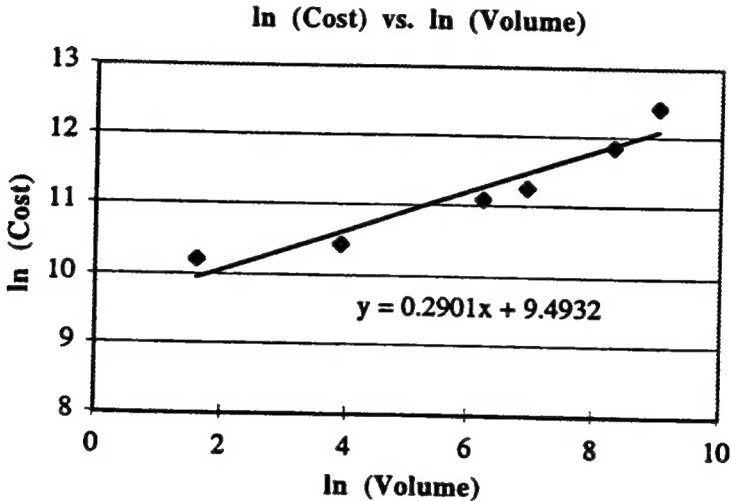
Review of Definitions and Assumptions	1,5,6,7,8,9
Introduction to the CD-ROM	17,18,A
Make a calculation	10,11,12,13
Open-ended	14,15,16
Straight forward	2(b),3,13
Fairly straight forward	4,11,12,B
More difficult	10

Chapter 1

P1-1 No solution will be given.

P1-2

- (a) Reactants might not be hot enough to react.
- (b) Plot Cost vs. Volume on log-log paper. Use this graph to generate an equation for cost as a function of volume.



From this we generate the equation : $\text{Cost} = 13,270(V)^{0.29}$

We can use this equation to find the desired prices:

For a 6000 gallon reactor : $\text{Cost} = 13,270(6000)^{0.29} = \$165,400$

For a 15,000 gallon reactor : $\text{Cost} = 13,270(15,000)^{0.29} = \$215,740$

(c)
$$V = \frac{10 \text{ dm}^3/\text{min}}{0.23 \text{ min}} \ln \frac{C_{A0}}{0.001 C_{A0}} = 300.3 \text{ dm}^3$$

(d) For Constant Pressure:

$$r_A = \frac{1}{V} \frac{dN_A}{dt} = \frac{1}{V} \frac{d(C_A V)}{dt} = \frac{dC_A}{dt} + \frac{C_A}{V} \frac{dV}{dt}$$

$$r_A = \frac{dC_A}{dt} + \frac{C_A}{V_0 + V_1 \sin(\omega t)} \omega V_1 \cos(\omega t)$$

- (e) He/She might not be able to respond to a malfunction if he/she became injured, and no one would be there to come to his/her aid.

P1-3. For a CSTR, equation (S1-3) is

$$V = \frac{F_{A0} - F_A}{-r_A}$$

where $-r_A = kC_A$

$$F_A = C_A V$$

So the first equation becomes

$$V = \frac{C_{A0}V - C_A V}{kC_A}$$

given that $C_A = 0.1 C_{A0}$, $v = 10 \text{ dm}^3/\text{min}$ and $k = 0.23/\text{min}$.

$$V = \frac{C_{A0}V - 0.1 C_{A0}V}{k(0.1)C_{A0}} = \frac{0.9V}{0.1k} = \frac{9(10 \text{ dm}^3/\text{min})}{0.23/\text{min}} = 391.3 \text{ liters}$$

The CSTR is 4 times larger than the plug flow reactor for these conditions.

Solution

Reaction: $A \longrightarrow B$

Problem: Determine time to reduce the number of moles of A to 1% of its initial value.

Mole Balance: (constant volume, batch reactor)

$$\frac{dN_A}{dt} = r_A V$$

Rate Law: (first order)

$$-r_A = kC_A, \text{ where } k = 0.23/\text{min} \text{ and } C_A = \frac{N_A}{V}$$

$$\text{Therefore, } -r_A = k \frac{N_A}{V}$$

Combine:

$$\frac{dN_A}{dt} = -kN_A$$

$$\int_0^t dt = -\frac{1}{k} \int_{N_{A0}}^{N_A} \frac{dN_A}{N_A}$$

$$t = -\frac{1}{k} \left[\ln \frac{N_A}{N_{A0}} \right] = -\frac{1}{k} \left[\ln \frac{0.01 N_{A0}}{N_{A0}} \right]$$

$$t = -\frac{1}{(0.23/\text{min})} [\ln 0.01]$$

$$t = 20.0 \text{ min.}$$

(Solution by J.T. Santini, Jr.)

P1-5.

- a) The assumptions made in deriving the design equation for a batch reactor are:
- closed system: no streams carrying mass enter or leave the reactor
 - no spatial variation in system properties
- b) The assumptions made in deriving the design equation for a CSTR, are:
- steady state
 - no spatial variation in concentration, temperature, or reaction rate through the vessel.
- c) The assumptions made in deriving the design equation for a plug-flow reactor are:
- steady state
 - no radial variation in properties of system.
- d) The assumptions made in deriving the design equation for a packed-bed reactor are:
- steady state
 - no radial variation in properties of system.
- e) $-r_A'$ is the rate of disappearance of species A per unit mass (or area) of catalyst [=] moles / (time-mass catalyst). r_A' is the rate of formation of species A per unit mass (or area) of catalyst [=] moles / (time-catalyst). $-r_A$ is an intensive quantity, in that it is a function of the concentration, temperature, pressure, and the type of catalyst (if any), and is defined at any point within the reactor. An extensive quantity is a property which is obtained by summing up the properties of individual subsystems within the total system; in this sense, $-r_A$ is independent of the 'extent' of the system.

P1-6

General Mole Balance:

$$\frac{dN_j}{dt} = F_{j0} - F_j + \int r_j dV$$

For a CSTR, there is no accumulation. Also, assume well mixed, so that there is no spatial variation in the reactor. The mole balance simplifies to:

$$0 = F_{j0} - F_j + r_j V$$

The rate of reaction based on volume is related to the rate of reaction based on catalyst weight by the bulk catalyst density ρ_b . The reactor volume and catalyst weight are also related by a similar equation.

$$\begin{aligned} -r_j &= \rho_b (-r_j') \\ W &= V \rho_b \end{aligned}$$

Combining and rearranging the last three equations gives the equation for a "fluidized" CSTR:

$$W = \frac{F_{j0} - F_j}{-r_j}$$

(Solution by J.T. Santini, Jr.)

P1-7. Mole balance on species j is:

$$F_{j0} - F_j + \int_0^V r_j dV = \frac{dN_j}{dt} \quad (1-4)$$

let M_j = mol. wt. of species j

Then $F_{j0} M_j = w_j$ [=] $\frac{(\text{moles})}{(\text{time})} \frac{(\text{mass})}{(\text{mole})}$ = mass flow rate of j into the reactor:

$$N_j M_j = m_j \text{ [=] } \frac{(\text{moles})}{(\text{mole})} \frac{(\text{mass})}{(\text{mole})} = \text{mass of species j in the reactor}$$

Multiplying Eqn. (1-4) by M_j

$$F_{j0} M_j - F_j M_j + M_j \int_0^V r_j dV = M_j \frac{dN_j}{dt} \quad (1-4a)$$

and noting that M_j is constant:

$$M_j \int_0^V r_j dV = \int_0^V r_j M_j dV \quad ; \quad M_j \frac{dN_j}{dt} = \frac{d(M_j N_j)}{dt}$$

Or, upon substitution into Eqn. (1-4a)

$$F_{j0} M_j - F_j M_j + \int_0^V M_j r_j dV = \frac{d}{dt} (M_j N_j) = \frac{d}{dt} (m_j)$$

$$w_{j0} - w_{jF} + \int_0^V M_j r_j dV = \frac{dm_j}{dt}$$

P1-8. No solution will be given.

Simpler Batch	Reactor is charged via two holes in the top of the tank; while reaction is carried out, nothing else is put in or taken out until the reaction is done; tank easily heated or cooled by jacket	<ol style="list-style-type: none"> 1. Gas phase 2. Liquid phase 3. Liquid solid 4. Fermentation 	<ol style="list-style-type: none"> 1. Small scale production 2. Intermediate or one shot production 3. Pharmaceutical 	<ol style="list-style-type: none"> 1. High conversion per unit volume for one pass 2. Flexibility of operation- same reactor can produce one product one time and a different product the next 3. Easy to clean 	<ol style="list-style-type: none"> 1. High operating cost 2. Product quality more variable than with continuous operation
Semi Batch	Either one reactant is charged and the other is fed continuously (at small concentrations) or else one of the product can be removed continuously (ie. avoid side reactions)	<ol style="list-style-type: none"> 1. Two phase rxns 2. Gas-liquid 3. Liquid-solid 	<ol style="list-style-type: none"> 1. Small scale production 2. Compelling reactions 	<ol style="list-style-type: none"> 1. High conversion per unit volume for one run 2. Good selectivity; feed can be controlled as to minimize side rxns 3. Flexibility of operation; can be used with a reflux condenser for solvent recovery, or in bubble type rxns 	<ol style="list-style-type: none"> 1. High operating labor cost 2. Product quality more variable than with continuous operation
Continuously Stirred Tank Reactor (CSTR)	Run at steady state with continuous flow of reactants and products; the feed assumes a uniform composition throughout the reactor, exit stream has the same composition as in the tank	<ol style="list-style-type: none"> 1. Liquid phase 2. Gas-liquid rxns 3. Solid-liquid rxns 	<ol style="list-style-type: none"> 1. When agitation is required 2. Series configurations for different concentration streams 	<ol style="list-style-type: none"> 1. Continuous operation 2. Good temperature control 3. Easily adapts to two phase rxns 4. Good control 5. Simplicity of construction 6. Low operating (labor) cost 7. Easy to clean 	<ol style="list-style-type: none"> 1. Lowest conversion per unit volume 2. By-passing and channeling possible with poor agitation
Pulsing Flow Reactor (PFR)	Arranged as one long long reactor or many short reactors in a tube bank; no radial variation in reaction rate (concentration); concentration changes with length down the reactor	<ol style="list-style-type: none"> 1. Primarily gas phase 	<ol style="list-style-type: none"> 1. Large scale 2. Fast reactions 3. Homogeneous rxns 4. Heterogeneous rxns 5. Continuous production 6. High temperature 	<ol style="list-style-type: none"> 1. High conversion per unit volume 2. Low operating (labor) cost 3. Continuous operation 4. Good heat transfer 	<ol style="list-style-type: none"> 1. Undesired thermal gradients may exist 2. Poor temperature control 3. Shutdown and cleaning may be expensive
Tubular fixed bed Reactor	Tubular reactor that is packed with solid catalyst particles	<ol style="list-style-type: none"> 1. Gas phase/solid catalyzed 2. Gas-solid rxns 	<ol style="list-style-type: none"> 1. Used primarily in heterogeneous rxns 1. Heterogeneous rxns with a catalyst 	<ol style="list-style-type: none"> 1. High conversion per unit mass of catalyst 2. Low operating cost 3. Continuous operation 	<ol style="list-style-type: none"> 1. Undesired thermal gradients may exist 2. Poor temperature control 3. Channeling may occur 4. Unit may be difficult to service and clean
Fluidized Bed Reactor	Heterogeneous reactions; like a CSTR in that the reactants are well mixed	<ol style="list-style-type: none"> 1. Gas-solid 2. Gas-solid catalyzed 	<ol style="list-style-type: none"> 1. Heterogeneous rxns with a catalyst 	<ol style="list-style-type: none"> 1. Good mixing 2. Good uniformity of temperature 3. Catalyst can be continuously regenerated with the use of an auxiliary loop 	<ol style="list-style-type: none"> 1. Bad fluid mechanics not well known 2. Severe agitation can result in catalyst destruction and dust formation 3. Uncertain scale-up

P1-10

Given: Los Angeles Basin: A = Basin area = $2 \times 10^{10} \text{ ft}^2$, H_i = Inversion height = 2000 ft, $V = 4 \times 10^{13} \text{ ft}^3$. Basin may be considered 'well-mixed'.

v_o wind from Mojave Desert $T = 75^\circ\text{F}$ and $P_o = 1.0 \text{ atm}$

$F_{\text{CO,A}}$ = CO emission from autos $F_{\text{CO,S}}$ = CO in Santa Ana wind

$Y_{\text{CO,A}} = 0.02$

$C_{\text{CO,S}} = 2.04 \times 10^{-10} \text{ lbmol/ft}^3$

$V_A = 3000 \text{ ft}^3/\text{car}$ at STP

C = number of cars = 400,000

1. N_B = no. of lb moles gas in system:

$$\frac{P_o V}{RT} = \frac{(1.0 \text{ atm})(4 \times 10^{13})}{(0.7302 \text{ atm} \cdot \text{ft}^3/\text{lbmol} \cdot ^\circ\text{R})(535^\circ\text{R})} = 1.024 \times 10^{11}$$

- 2.

$$F_{\text{CO,A}} = y_{\text{CO,A}} V_A C = (0.02 \text{ mol CO/mol gas})(3000 \text{ scf/hr} \cdot \text{car})(400,000 \text{ cars})(\text{lbmol}/390.66 \text{ scf})$$

$$F_{\text{CO,A}} = 6.143 \times 10^4 \text{ lbmol/hr}$$

3. v = wind speed = 15 mph W = corridor width = 20 miles

$$v_o = vWH_i = (15 \text{ mph})(20 \text{ miles})(2000 \text{ ft})(5280 \text{ ft/mile})^2$$

$$v_o = 1.67 \times 10^{13} \text{ ft}^3/\text{hr}$$

- 4.

$$F_{\text{CO,S}} = v_o C_{\text{CO,S}} = (2.04 \times 10^{-10} \text{ lbmol/ft}^3)(1.67 \times 10^{13} \text{ ft}^3/\text{hr})$$

$$F_{\text{CO,S}} = 3.407 \times 10^3 \text{ lbmol/hr}$$

5. CO Balance: Input to LA Basin from cars = $F_{\text{CO,A}}$, from the Santa Ana wind = $F_{\text{CO,S}}$;
Output = $v_o C_{\text{CO}}$, where C_{CO} = Concentration of CO in Basin.

$$\therefore F_{\text{CO,A}} + F_{\text{CO,S}} - v_o C_{\text{CO}} = V \frac{dC_{\text{CO}}}{dt}$$

6. At $t = 0$, $C_{\text{CO}} = C_{\text{CO,0}}$; rearranging and integrating above

$$\therefore \int_{C_{\text{CO,0}}}^{C_{\text{CO}}} \frac{dC_{\text{CO}}}{F_{\text{CO,A}} + F_{\text{CO,S}} - v_o C_{\text{CO}}} = \frac{-\ln}{v_o} \left[\frac{F_{\text{CO,A}} + F_{\text{CO,S}} - v_o C_{\text{CO}}}{F_{\text{CO,A}} + F_{\text{CO,S}} - v_o C_{\text{CO,0}}} \right] = \int_0^t \frac{dt}{V} = \frac{t}{V}$$

$$\therefore t = \frac{V}{v_o} \ln \left[\frac{F_{\text{CO,A}} + F_{\text{CO,S}} - v_o C_{\text{CO,0}}}{F_{\text{CO,A}} + F_{\text{CO,S}} - v_o C_{\text{CO}}} \right]$$

7. At 8 ppm, $C_{CO} = 2.04 \times 10^{-8}$ lb mole/ft³;

\therefore at 2 ppm, $C_{CO} = \frac{2}{8} \times 2.04 \times 10^{-8} \frac{\text{lbmole}}{\text{ft}^3}$

$C_{CO} = 0.51 \times 10^{-8}$ lb mole/ft³

$\therefore t = \frac{4 \times 10^{13} \text{ ft}^3}{1.67 \times 10^{13} \text{ hr}} \ln(A)$ where

$$A = \left[\frac{6.685 \times 10^4 \frac{\text{lbmole}}{\text{hr}} + 3.407 \times 10^3 \frac{\text{lbmole}}{\text{hr}} - 2.04 \times 10^{-8} \frac{\text{lbmole}}{\text{ft}^3} \times 1.67 \times 10^{13} \frac{\text{ft}^3}{\text{hr}}}{6.685 \times 10^4 \frac{\text{lbmole}}{\text{hr}} + 3.407 \times 10^3 \frac{\text{lbmole}}{\text{hr}} - 0.51 \times 10^{-8} \frac{\text{lbmole}}{\text{ft}^3} \times 1.67 \times 10^{13} \frac{\text{ft}^3}{\text{hr}}} \right]$$

$$t = \frac{4 (\text{hr})}{1.67} \ln \left[\frac{6.685 \times 10^4 + 3.407 \times 10^3 - 3.407 \times 10^5}{6.685 \times 10^4 + 3.407 \times 10^3 - .8517 \times 10^5} \right] = \frac{4}{1.67} \ln \left[\frac{2.705}{1.492} \right] \text{ hr.}$$

$$= 1.42 \text{ hr.}$$

For NO:

2. $C_{NO,A} = 3.84 \times 10^{-6}$ lb mole/ft³ $\therefore F_{NO,A} = C_{NO,A} v_A C$

$F_{NO,A} = 3.84 \times 10^{-6} \text{ lb mole/ft}^3 \times 3000 \text{ ft}^3/\text{hr. car}$
 $\times 400,000 \text{ cars} = 4.608 \times 10^3 \text{ lb mole/hr}$

3. $v_o = 1.67 \times 10^{13} \text{ ft}^3/\text{hr}$ (same as for CO)

4. $F_{AO,S} = 0$ (given)

5. NO material balance becomes, with $F_{NO,S} = 0$

$$F_{NO,A} - v_o C_{NO} = v \frac{dC_{NO}}{dt} \quad C_{NO,O} = 0.5 \text{ ppm} = \frac{0.5 \text{ ppm}}{8 \text{ ppm}} \times 2.04 \times 10^{-8} \frac{\text{lbmole}}{\text{ft}^3}$$

$$C_{NO,O} = .1275 \times 10^{-8} \text{ lb mole/ft}^3$$

6. Solution to D.E. is now

$$t = \frac{v}{v_o} \ln \left[\frac{F_{NO,A} - v_o C_{NO,O}}{F_{NO,A} - v_o C_{NO}} \right]$$

P1-10 (cont'd)

7. The lowest concentration of NO occurs when that taken away by the wind is just balanced by that produced by the autos, i.e. when

$$\frac{dC_{NO}}{dt} = 0 \quad \therefore \quad C_{NO,SS} = \frac{F_{NO,A}}{v_o} = \frac{4.608 \times 10^3 \frac{\text{lbmole}}{\text{hr}}}{1.67 \times 10^{13} \text{ft}^3/\text{hr}} = 2.759 \times 10^{-10} \frac{\text{lbmole}}{\text{ft}^3}$$

$$\text{with } C_{NO} = 0.1 \text{ ppm} = \frac{0.1 \text{ ppm}}{8 \text{ ppm}} \times 2.04 \times 10^{-8} \text{ lbmole/ft}^3 = 2.55 \times 10^{-10} \frac{\text{lbmole}}{\text{ft}^3}$$

It is seen that this is less than $C_{NO,SS}$. \therefore The concentration of NO will never reach 0.1 ppm unless L.A.'s driving habits are altered.

P1-11. Solution

Reaction: $A \longrightarrow B$
constant volumetric flowrate; isothermal; continuous flow reactor

$$F_{Ao} = 5.0 \text{ mol/hr}, v_o = 10 \text{ dm}^3/\text{hr} \longrightarrow C_{Ao} = 0.5 \text{ mol/dm}^3$$

$$(a) -r_A = k, \text{ with } k = 0.05 \frac{\text{mol}}{\text{hr dm}^3}$$

CSTR

$$\text{Mole Balance: } V = \frac{F_{Ao} - F_A}{-r_A}$$

$$\text{Rate Law: } -r_A = k = 0.05 \frac{\text{mol}}{\text{hr dm}^3}$$

$$\text{Combine: } V = \frac{F_{Ao} - 0.01 F_{Ao}}{-r_A} = \frac{\left(5 \frac{\text{mol}}{\text{hr}}\right)(0.99)}{\left(0.05 \frac{\text{mol}}{\text{hr dm}^3}\right)} = 99.0 \text{ dm}^3$$

$$\text{Volume of the CSTR} = \underline{99.0 \text{ dm}^3}$$

PFR

Mole Balance: $\frac{dF_A}{dV} = r_A$

Rate Law: $-r_A = k = 0.05 \frac{\text{mol}}{\text{hr dm}^3}$

Combine: $\frac{dF_A}{dV} = -k$

$$-\frac{1}{k} \int_{F_{A0}}^{F_A} dF_A = \int_0^V dV$$

$$V = -\frac{1}{k} [0.01 F_{A0} - F_{A0}] = -\frac{\left(5 \frac{\text{mol}}{\text{hr}}\right)}{\left(0.05 \frac{\text{mol}}{\text{hr dm}^3}\right)} (-0.99)$$

Volume of PFR = 99.0 dm³

(b) $-r_A = kC_A$ with $k = 0.0001 \text{ s}^{-1}$

CSIR

Mole Balance in terms of concentration: $V = \frac{v_0(C_{A0} - C_A)}{-r_A}$

Rate Law: $-r_A = kC_A$

$$\text{Combine: } V = \frac{v_0(C_{A0} - 0.01C_{A0})}{k(0.01)(C_{A0})} = \frac{\left(10 \frac{\text{dm}^3}{\text{hr}}\right)(0.99)}{\left(\frac{0.0001}{\text{s}}\right)(0.01)\left(\frac{3600 \text{ s}}{\text{hr}}\right)}$$

$$V = 2750 \text{ dm}^3$$

PFR

Mole Balance in terms of concentration: $\frac{dC_A}{dV} = \frac{r_A}{v_0}$

Rate Law: $-r_A = kC_A$

$$\text{Combine: } \int_0^V dV = -\frac{v_0}{k} \int_{C_{A0}}^{0.01C_{A0}} \frac{dC_A}{C_A}$$

$$V = -\frac{v_0}{k} \left[\ln \frac{0.01 C_{A0}}{C_{A0}} \right] = \frac{-\left(10 \frac{\text{dm}^3}{\text{hr}}\right)}{\left(\frac{0.0001}{\text{s}}\right)\left(\frac{3600 \text{ s}}{\text{hr}}\right)} \ln(0.01)$$

Volume of PFR = 128.0 dm³

(c) $-r_A = kC_A^2$, with $k = 3.0 \frac{\text{dm}^3}{\text{mol hr}}$

CSTR

Mole Balance in terms of concentration: $V = \frac{v_o(C_{Ao} - C_A)}{-r_A}$

Rate Law: $-r_A = kC_A^2$

Combine: $V = \frac{v_o(C_{Ao} - 0.01C_{Ao})}{k(0.01C_{Ao})^2} = \frac{(0.99)\left(10 \frac{\text{dm}^3}{\text{hr}}\right)}{\left(3.0 \frac{\text{dm}^3}{\text{mol hr}}\right)(0.0001)\left(0.5 \frac{\text{mol}}{\text{dm}^3}\right)}$

Volume of CSTR = 66,000 dm³

PFR

Mole Balance in terms of concentration: $\frac{dC_A}{dV} = \frac{r_A}{v_o}$

Rate Law: $-r_A = kC_A^2$

Combine: $\int_0^V dV = -\frac{v_o}{k} \int_{C_{Ao}}^{0.01C_{Ao}} \frac{dC_A}{C_A^2} = -\frac{v_o}{kC_{Ao}} \left[-\frac{1}{0.01} + 1 \right]$

$V = -\frac{\left(10 \frac{\text{dm}^3}{\text{hr}}\right)}{\left(3.0 \frac{\text{dm}^3}{\text{mol hr}}\right)\left(0.5 \frac{\text{mol}}{\text{dm}^3}\right)} [-99.0]$

Volume of PFR = 660 dm³

(Solution by J.T. Santini, Jr.)

Solution

Reaction: $A \longrightarrow B + C$
 isothermal; well-mixed; constant volume batch reactor
 $V = 20 \text{ dm}^3$, $N_{A0} = 20 \text{ moles}$

(a) $-r_A = kC_A$, with $k = 0.865 \text{ min}^{-1}$

Mole Balance: (constant volume batch reactor)

$$\frac{dC_A}{dt} = r_A$$

Rate Law: $-r_A = kC_A$

Combine: $\frac{dC_A}{dt} = -kC_A$

$$\int_0^t dt = -\frac{1}{k} \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A}$$

$$t = -\frac{1}{k} \ln \left[\frac{N_A}{N_{A0}} \right] = -\frac{1}{0.865 \text{ min}^{-1}} \ln \left[\frac{0.2}{20} \right]$$

$$t = \underline{5.3 \text{ min.}}$$

(b) $-r_A = kC_A^2$, with $k = \frac{2 \text{ dm}^3}{\text{mol} \cdot \text{min}}$

Mole Balance: $\frac{dC_A}{dt} = r_A$

Rate Law: $-r_A = kC_A^2$

Combine: $\frac{dC_A}{dt} = -kC_A^2$

$$\int_0^t dt = -\frac{1}{k} \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^2}$$

$$t = -\frac{1}{k} \left[-\frac{1}{C_A} + \frac{1}{C_{A0}} \right] = -\left(\frac{2 \text{ dm}^3}{\text{mol} \cdot \text{min}} \right)^{-1} \left[-\left(\frac{0.05 \text{ mol}}{\text{dm}^3} \right)^{-1} + \left(\frac{1 \text{ mol}}{\text{dm}^3} \right)^{-1} \right]$$

$$t = \underline{9.5 \text{ min.}}$$

(c) Assume Ideal Gas Equation Holds

Temperature = $127^\circ\text{C} = 400\text{K}$ (constant because isothermal)

Volume = 20 dm^3 (constant)

Initial Total Moles = 20

Final Total Moles = 40 (reaction goes to completion)

Gas Constant = $0.082 \frac{\text{dm}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}}$

Initial Pressure:

$$P_0 = \frac{nRT}{V} = \frac{(20 \text{ moles})(0.082)(400\text{K})}{(20 \text{ dm}^3)}$$

$$P_0 = \underline{32.8 \text{ atm}}$$

Final Pressure:

$$P_f = \frac{nRT}{V} = \frac{(40 \text{ moles})(0.082)(400\text{K})}{(20 \text{ dm}^3)}$$

$$P_f = \underline{65.6 \text{ atm}}$$

P1-13. PBR

The volumetric flow rate is given as $v_{O1} = 30,000 \text{ m}^3/\text{hr}$ at $T_1 = 513\text{K}$ and $P_1 = 27 \text{ atm}$. The ideal gas law is used to determine the volumetric flow rate, v_{O2} , at STP.

$$\frac{v_{O1} P_1}{T_1} = \frac{v_{O2} P_2}{T_2}$$

Solving for v_{O2} yields:

$$v_{O2} = \frac{v_{O1} P_1 T_2}{T_1 P_2} = \frac{30,000 \frac{\text{m}^3}{\text{hr}} * 298\text{K} * 27\text{atm}}{513\text{K} * 1\text{atm}} * \left(\frac{1\text{ft}}{3048\text{m}}\right)^3 * \frac{1\text{hr}}{3600\text{sec}} = 4616 \frac{\text{ft}^3}{\text{sec}}$$

In order to find the residence time of each molecule, we will first calculate the gas velocity, u , in each tube (where N is the total number of tubes and AC is the cross sectional area of each tube).

$$u = \frac{v_{O1}}{NA_c} = \frac{30,000 \frac{\text{m}^3}{\text{hr}}}{2050 * 5.89 * 10^{-4} \text{m}^2} = 24,846 \frac{\text{m}}{\text{hr}} = 6.90 \frac{\text{m}}{\text{sec}}$$

The residence time can now be calculated using the gas velocity and the length, L , of each tube.

$$\tau = \frac{L}{u} = \frac{12\text{m}}{6.90 \frac{\text{m}}{\text{sec}}} = 1.75\text{sec}$$

STTR

$$u = \frac{v_{O1}}{A_c} = \frac{300,000 \frac{\text{m}^3}{\text{hr}}}{9.62\text{m}^2} = 31,191.4 \frac{\text{m}}{\text{hr}} = 8.66 \frac{\text{m}}{\text{sec}}$$

$$\tau = \frac{L}{u} = \frac{38\text{m}}{8.66 \frac{\text{m}}{\text{sec}}} = 4.4\text{sec}$$

$$P_{\text{catalyst}} = \frac{m}{V} = \frac{150,000\text{kg}}{38\text{m} * 9.62\text{m}^2} = 410.3 \frac{\text{kg}}{\text{m}^3}$$

P1-14. No solution will be given.

P1-15. a) Chemical Marketing Report, Chemical Week

b) Chemical Process Industries (R.N. Shreve, J.A. Brink, Jr., 4th ed., New York - McGraw - Hill Book Co., Inc., 1977), Industrial and Engineering Chemistry.

P1-16. A typical catalytic cracking reactor used in petroleum refining operates at 885-1020°F and 10-30 psig. Chemical Process Industries, R.C. Shreve and J.A. Brink, Jr., 4th ed., New York - McGraw - Hill Book Co., Inc., 1977, p. 675.

P1-17. No solution will be given

P1-18. P1-18 (a)

Equations:

$$d(x)/d(\tau) = k_1 \cdot x - k_2 \cdot x \cdot y$$

$$d(y)/d(\tau) = k_3 \cdot x \cdot y - k_4 \cdot y$$

$$k_1 = .02$$

$$k_2 = .00004$$

$$k_3 = .00004$$

$$k_4 = .04$$

$$\tau_0 = 0, \quad \tau_f = 800$$

Initial value

500

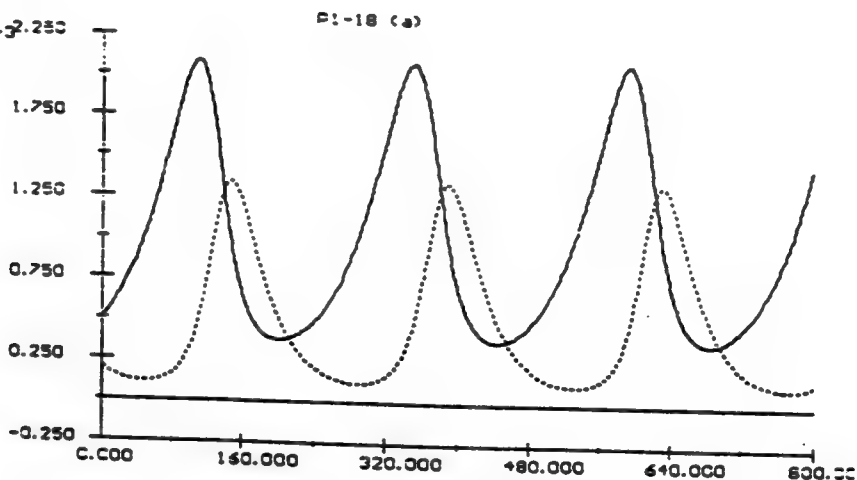
200

Scale: $10^{-2.250}$

KEY:

-x

--y



P1-18 (b)

Equations:

$$f(x) = x^{*3} \cdot y - 4 \cdot y^{*2} + 3 \cdot x - 1$$

$$f(y) = 6 \cdot y^{*2} - 9 \cdot x \cdot y - 5$$

Initial value

2

2

P1-18 (b)
Solution

Variable	Value	f()
x	2.38504	2.292e-14
y	3.79703	-2.55e-15

P1-19. No solution will be given

1-16

CDP1-A

a) Find number of moles and concentration

$$n = \frac{PV}{RT} = \frac{(20 \text{ atm})(200 \text{ dm}^3)}{\left(8.3145 \frac{\text{kJ}}{\text{molK}}\right)(500 \text{ K})} \left(\frac{101.33 \text{ kPa}}{1 \text{ atm}}\right) = 97.5 \text{ moles}$$

$$\text{moles A} = .75 * 97.5 = 73.1 \text{ moles A}$$

$$C_A = \frac{\text{moles}}{\text{volume}} = \frac{73.1 \text{ moles}}{200 \text{ dm}^3} = 0.37 \text{ moles A}$$

b) Determine reaction time

$$\frac{dN_A}{dt} = r_A V$$

$$\frac{dN_A}{dt} = -k N_A$$

$$\int_{73.1}^{.731} \frac{dN_A}{N_A} = -k \int_0^t dt$$

$$\ln .731 - \ln 73.1 = -.1t$$

$$t = 23 \text{ min}$$

c) Determine reaction time

$$\frac{dN_A}{dt} = r_A V$$

$$C_A = \frac{N_A}{V}$$

$$\frac{dC_A}{dt} = -k C_A^2$$

$$\int_{.37}^{.074} \frac{dC_A}{C_A^2} = -k \int_0^t dt$$

$$-10.8 = -0.7t$$

$$t = 15 \text{ min}$$

CDP1-B Given: Liquid phase reaction $A \rightarrow B$ in a foam reactor:

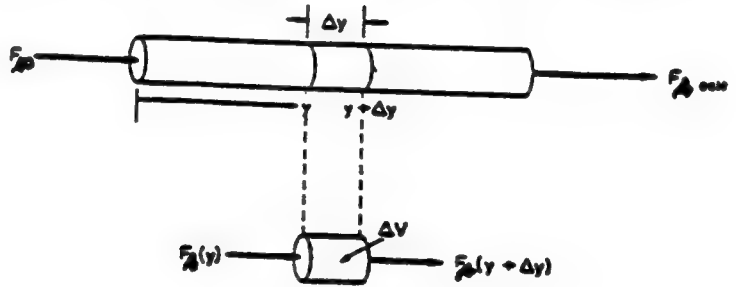


Figure P1-10.

Consider a differential element, ΔV of the reactor:

By material balance $F_A - (F_A + \Delta F_A) = -r_A(1-e)\Delta V$

where $(1-e)\Delta V$ = fraction of reactor element which is liquid.

Or:

$$-\Delta F_A = (-r_A)(1-e)\Delta V$$

$$\therefore \frac{dF_A}{dV} = r_A(1-e) \quad \text{Must relate } (-r_A) \text{ to } F_A,$$

where F_A is the total (gas + liquid) molar flow rate of A.

$-r_A$ = rate of reaction (gmoles A per cu cm of liquid per sec)

e = volume fraction of gas

F_A = molar flow rate of A (gmoles/sec)

V = volume of reactor

Chapter 2

General: The overall goal of these problems is to help the student realize that if they have $-r_A=f(X)$ they can "design" or size a large number of reaction systems. It sets the stage for the algorithm developed in Chapter 4.

- P2-1.** This problem will keep students thinking about writing down what they learned every chapter.
- P2-2.** Part (a) is open-ended and encourages the student to do little "OUT OF THE BOX" thinking.
- P2-3.** Straight forward rehash of Example 2-7 to calculate reactor volumes.
- P2-4.** Uses definition of space time to calculate V. Can be done in 30 seconds.
- P2-5.** No calculations necessary for this problem, but does require some thinking.
- P2-6.** This problem encompasses most all the key points of Chapter 2. That is, if we are given $-r_A=f(X)$ then we can size any number of reactor systems. Some parts plug and chug, others require more thinking.
- P2-7.** Good troubleshooting problem. Could ask the students to brainstorm in groups what could have happened.

Problems P2-8, P2-9, and P2-12 are alternative problems to P2-6 and can be assigned in different years.

P2-10. The point is to estimate the sizes of these real reactors. The students can use the door as a point of reference to estimate the reactor volumes. Could be used with the ethical dilemma problems. CDP2-B.

P2-11. Open-ended in that student is faced with decision on how to relax.

P2-13. In recent years, a number of students have on their own fit a polynomial to the curves in P2-6, P2-8, P2-9, and P2-12 and then used POLYMATH to solve the problems.

Problems P2-14 and P2-15 encourage outside reading and help to develop life-long learning skills by obtaining information on their own.

CDP2-A Similar to 2-9

CDP2-B Good problem to get groups started working together (e.g. cooperative learning).

CDP2-C Similar to problems 2-8, 2-9, 2-12.

CDP2-D Similar to problems 2-8, 2-9, 2-12.

Summary

	<u>Assigned</u>	<u>Alternates</u>	<u>Difficulty</u>	<u>Time</u>	<u>Solution Given</u>
P2-1	O			5	No
P2-2	O		OE	30	No
P2-3	I			15	Yes
P2-4	O			10	Yes
P2-5	O		M	40	Yes
● P2-6		8,12	SF	20	Yes
● P2-7		6,8,12	M	45	Yes
P2-8	AA	6,7,12	FSF	50	Yes
P2-9	O	A,B,D	SF	60	Yes
P2-10	S		SF	20	No
● P2-11			SF		Yes
P2-12	AA	6,7,8	SF	60	Yes
P2-13	S		M	30	No
P2-14	S			60	No
P2-15	S			30	No
CDP2-A	O	9,B,C,D	FSF	45	Yes
CDP2-B	O	9,B,C,D	FSF	15	No
CDP2-C	O	9,B,C,D		10	Yes
CDP2-D	O	9,B,C,D		10	Yes

Assigned

- = Always assigned, AA = Always assign one from the group of alternates, O = Often, I = Infrequently, S = Seldom, G = Graduate level

Alternates

In problems that have a dot in conjunction with AA means that one of the problems, either the problem with a dot or any one of the alternates are always assigned.

Time

Approximate time in minutes it would take a B/B* student to solve the problem.

Difficulty

- SF = Straight forward reinforcement of principles (plug and chug)
- FSF = Fairly straight forward (requires some manipulation of equations or an intermediate calculation).
- IC = Intermediate calculation required
- M = More difficult
- OE = Some parts open-ended.

*Note the letter problems are found on the CD-ROM. For example A \equiv CDP1-A.

Summary Table Ch-2

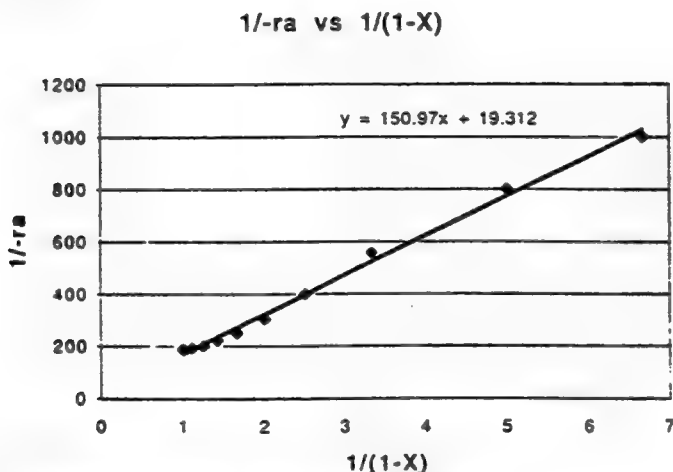
Straight forward	3,4,6
Fairly straight forward	8,11
More difficult	5,7,13
Open-ended	2(a),2(b),7,10,11,14,15, B
Comprehensive	2,3,4,5,6
Parameter sensitivity	—
Critical thinking	5(d),9(a)

Chapter 2

P2-1 No solution will be given.

P2-2

- (a) Plotting the given data as $1/-r_A$ vs. $1/(1-X)$ produces a linear graph. This can be used to extrapolate values for $-r_A$ for all of the conversion values up to the desired 0.98. These values can be used to calculate the desired volume.



The following equation was found to fit the data:

$$\frac{1}{-r_A} = 19.312 + \frac{150.97}{(1-X)}$$

Graphing $1/-r_A$ vs. $1/(1-X)^2$ proved to be non-linear.

- (b) One cannot extrapolate to a higher temperature unless the activation energy is given.

P2-3

a) Scheme A

$$\begin{aligned}
 V_1 &= F_{A0} \int_0^{0.3} \frac{dX}{-r_A} = F_{A0} \left[\frac{1}{2} \left(\frac{1}{-r_A(X=0)} + \frac{1}{-r_A(X=0.3)} \right) \right] \\
 &= 52 \frac{\text{mol}}{\text{min}} \times \frac{1 \text{ min}}{60 \text{ s}} \left[\frac{0.3}{2} (200 + 250) \right] \frac{\text{dm}^3 \cdot \text{s}}{\text{mol}} \\
 &= 58.5 \text{ dm}^3
 \end{aligned}$$

$$V_2 = F_{A0} \frac{X_2 - X_1}{-r_A(X_2)} = \frac{52}{60} \left(\frac{0.8 - 0.3}{0.8} \right) (800)$$

$$V_{\text{Total}} = 58.5 + 346.7 = 405.0 \text{ dm}^3$$

P2-3 cont'd

Scheme B

$$V_1 = \frac{F_{A0} X_1}{-r_A} = \frac{52}{60} (0.3) (300) = 78 \text{ dm}^3$$

$$V_2 = F_{A0} \int_0^X \frac{dX}{-r_A} = F_{A0} \frac{h}{3} \left[\frac{1}{-r_A(.3)} + \frac{4}{-r_A(.425)} + \frac{2}{-r_A(.55)} + \frac{4}{-r_A(.675)} + \frac{1}{-r_A(.8)} \right]$$

$$V_2 = \frac{52}{60} \left(\frac{125}{3} \right) [250 + 4(275) + 2(325) + 4(500) + 800]$$

$$V_2 = 173 \text{ dm}^3$$

$$V_{\text{Total}} = 78 \text{ dm}^3 + 173 \text{ dm}^3 = 251 \text{ dm}^3$$

b) Scheme A

$$V_1 = F_{A0} \frac{h}{3} \left[\frac{1}{-r_A(0)} + \frac{4}{-r_A(.35)} + \frac{1}{-r_A(.7)} \right]$$

$$= \frac{52}{60} \frac{(.35)}{3} [200 + 4(265) + 550] = 183 \text{ dm}^3$$

$$V_2 = \frac{52}{60} (.8 - .7) (800) = 69.3 \text{ dm}^3$$

$$V_{\text{Total}} = 252 \text{ dm}^3$$

Scheme B

$$V_1 = \frac{52}{60} (.7) (550) = 333.7 \text{ dm}^3$$

$$V_2 = \frac{52}{60} \frac{0.10}{2} [550 + 800] = 58.5 \text{ dm}^3$$

$$V_{\text{Total}} = 392 \text{ dm}^3$$

P2-3 cont'd

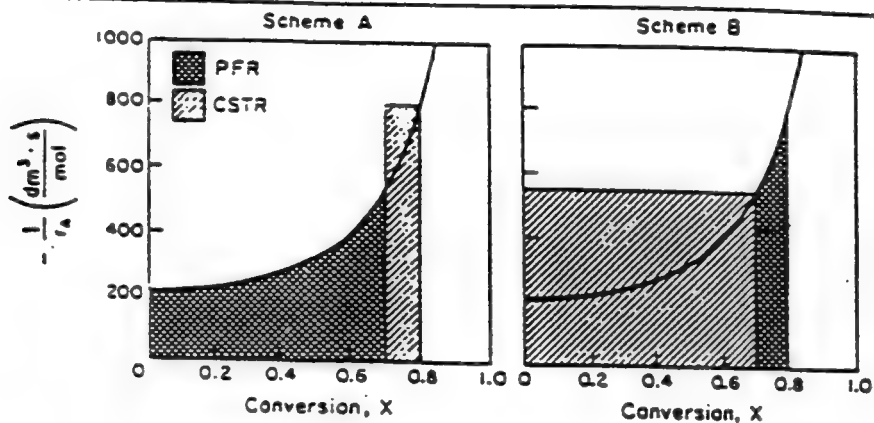


Figure E2-6.2

P2-4. Given: $t = 5$ hrs. to achieve $X = 0.8$ in a CSTR;

$$v_0 = 2 \text{ ft}^3/\text{min.}$$

$$V = t v_0 = (5 \text{ hrs}) \left[\frac{2 \text{ ft}^3}{\text{min}} \right] \left[\frac{60 \text{ min}}{\text{hr}} \right] = 600 \text{ ft}^3 \quad \underline{\text{ans.}}$$

$$SV = \frac{1}{t} = \frac{1}{5 \text{ hr.}} = 0.2 \text{ hr}^{-1}$$

P2-5

$$-r_A = kC_A^2 = kC_{A0}^2(1-X)^2$$

System 1:

CSTR

$$V = \frac{F_{A0} X_{\text{exit}}}{-r_A} = \frac{F_{A0} X_{\text{exit}}}{kC_{A0}^2(1-X_{\text{exit}})^2}$$

$$(1-X_{\text{exit}})^2 = \frac{F_{A0}}{VkC_{A0}^2} X_{\text{exit}} = aX_{\text{exit}}$$

P2-5 cont'd

$$\text{where } a = \frac{F_{Ao}}{V k C_{Ao}^2}$$

$$X_{\text{exit}}^2 - (2+a)X_{\text{exit}} + 1 = 0$$

$$X_{\text{exit}} = \frac{(2+a) - \sqrt{(2+a)^2 - 4}}{2} \quad \frac{(2+a) + \sqrt{(2+a)^2 - 4}}{2}$$

For the second root $X_{\text{exit}} \geq 1$, which is impossible. Hence,

$$X_{\text{exit}} = \frac{(2+a) - \sqrt{(2+a)^2 - 4}}{2} \quad (1)$$

PFR

$$V = \int_{X_{\text{exit}}}^{X_{OA}} \frac{dX}{k C_{Ao}^2 (1-X)^2} \Rightarrow 1 = a \left[\frac{1}{1-X} \right]_{X_{\text{exit}}}^{X_{OA}}$$

$$\frac{1}{1-X_{OA}} - \frac{1}{1-X_{\text{exit}}} = \frac{1}{a}$$

$$\frac{1}{1-X_{OA}} = \frac{1}{a} + \frac{1}{1 - \frac{(2+a) - \sqrt{a^2 + 4a}}{2}} = \frac{1}{a} + \frac{2}{\sqrt{a^2 + 4a} - a}$$

$$1 - X_{OA} = \frac{a(\sqrt{a^2 + 4a} - a)}{\sqrt{a^2 + 4a} + a} \Rightarrow X_{OA} = 1 - \frac{a(\sqrt{a^2 + 4a} - a)}{\sqrt{a^2 + 4a} + a}$$

$$\text{For } a = 1, \quad X_{OA} = 0.618$$

System 2:

PFR

$$V = \int_0^{X_{\text{exit}}} \frac{dX}{k C_{Ao}^2 (1-X)^2} = \frac{F_{Ao}}{k C_{Ao}^2} \left[\frac{1}{1-X} \right]_0^{X_{\text{exit}}}$$

$$\frac{1}{1-X_{\text{exit}}} - 1 = \frac{1}{a} \Rightarrow 1 - X_{\text{exit}} = \frac{a}{a+1}$$

$$X_{\text{exit}} = \frac{1}{1+a} \quad (2)$$

CSTR

$$V = \frac{F_{Ao}(X_{OA} - X_{\text{exit}})}{k C_{Ao}^2 (1-X_{OA})^2} \Rightarrow (1-X_{OA})^2 = a(X_{OA} - X_{\text{exit}})$$

P2-5 cont'd

$$X_{OA}^2 - (2+a)X_{OA} + \left(1 + \frac{a}{1+a}\right) = 0$$

$$X_{OA} = \frac{(2+a) - \sqrt{(2+a)^2 - 4\left(1 + \frac{a}{1+a}\right)}}{2}$$

$$X_{OA} = \frac{(2+a) - \sqrt{a^2 + 4a - \frac{4a}{1+a}}}{2}$$

$$\text{For } a=1, X_{OA} = 0.634$$

System 3:

CSTR

From Equation (1)

$$X_1 = \frac{(2+a/2) - \sqrt{a^2/4 + 2a}}{2}$$

PFR

From Equation (2)

$$X_2 = \frac{1}{1+a/2}$$

$$X_{OA} = \frac{X_1 + X_2}{2} = \frac{1}{2} \left(\frac{(2+a/2) - \sqrt{a^2/4 + 2a}}{2} + \frac{1}{1+a/2} \right)$$

$$\text{For } a=1, X_{OA} = 0.583$$

- (a) System 2 will give the highest conversion.
- (b) System 3 will give the lowest conversion.

Solution

X	0	0.2	0.4	0.6	0.8	0.9
$-r_A$	10	16.67	50	50	12.5	9.09
$1/-r_A$	0.1	0.06	0.02	0.02	0.8	0.11

(a) To solve this problem, first plot $1/-r_A$ vs. X from the chart above (see attached plot). Second, use mole balances as given below.

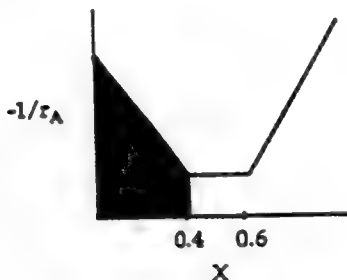
CSTR:

$$\text{Mole Balance: } V_{\text{CSTR}} = \frac{F_{A0} X}{-r_A} = \frac{\left(300 \frac{\text{mol}}{\text{min}}\right)(0.4)}{\left(50 \frac{\text{mol}}{\text{dm}^3 \cdot \text{min}}\right)}$$

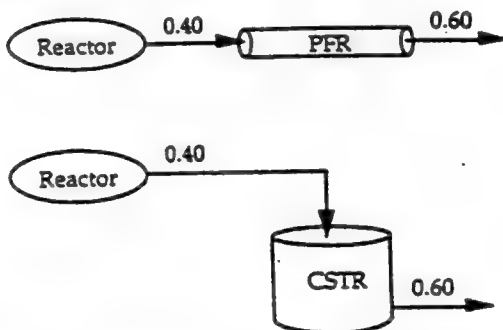
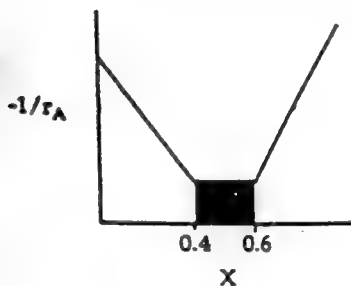
$$V_{\text{CSTR}} = \underline{2.4 \text{ dm}^3}$$

PFR:

$$\text{Mole Balance: } V_{\text{PFR}} = F_{A0} \int_0^X \frac{dX}{-r_A} = 300 [\text{area under the curve}] = \underline{7.2 \text{ dm}^3}$$



(b) For a feed stream that enters the reaction with a previous conversion of 0.40 and leaves at any conversion up to 0.60, the volumes of the PFR and CSTR will be identical because the rate is constant over this conversion range. (see below)



(Note: The reactor(s) before and up to achieving a conversion of 0.40 must be in series with no side streams.)

P2-6 cont'd

(c) $V_{\text{CSTR}} = 10.5 \text{ dm}^3$

Mole Balance: $V_{\text{CSTR}} = \frac{F_{A0} X}{-r_A}$

$$\frac{X}{-r_A} = \frac{V}{F_{A0}} = \frac{10.5 \text{ dm}^3}{300 \frac{\text{mol}}{\text{min}}} = 0.035 \frac{\text{dm}^3 \text{ min}}{\text{mol}}$$

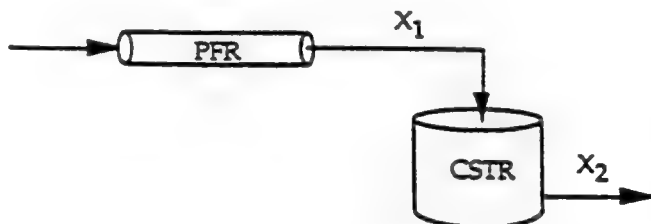
Use trial and error to find the maximum conversion.

First, pick a conversion. Second, find $1/-r_A$ from the plot. Third check to see if $X/-r_A$ is equal to 0.035. If it is, then the correct conversion has been chosen.

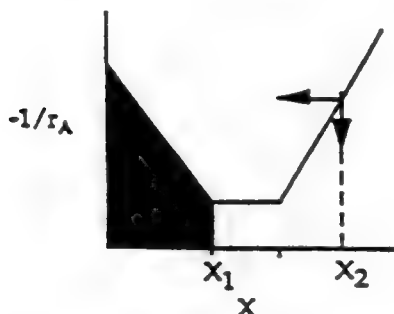
At $X = 0.70$, $\frac{1}{-r_A} = 0.05$, and $\frac{X}{-r_A} = 0.035 \frac{\text{dm}^3 \text{ min}}{\text{mol}}$

Maximum conversion = 0.70

(d)



From part (a), we know that $X_1 = 0.40$. Use trial and error to find X_2 .



P2-6 cont'd

Mole Balance: $V = \frac{F_{Ao}(X_2 - X_1)}{-r_A)_{X_1}}$

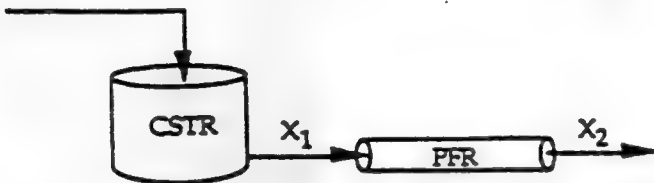
rearranging, we get

$$\frac{X_2 - 0.40}{-r_A)_{X_1}} = \frac{V}{F_{Ao}} = \frac{2.4}{300} = 0.008$$

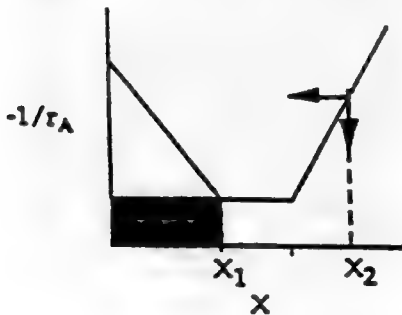
At $X_2 = 0.64$, $\frac{X_2 - 0.40}{-r_A)_{X_1}} = 0.008$

Conversion = 0.64

(e)



From part (a), we know that $X_1 = 0.40$. Use trial and error to find X_2 .



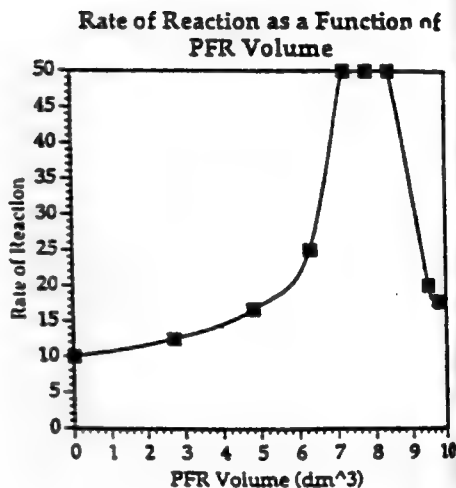
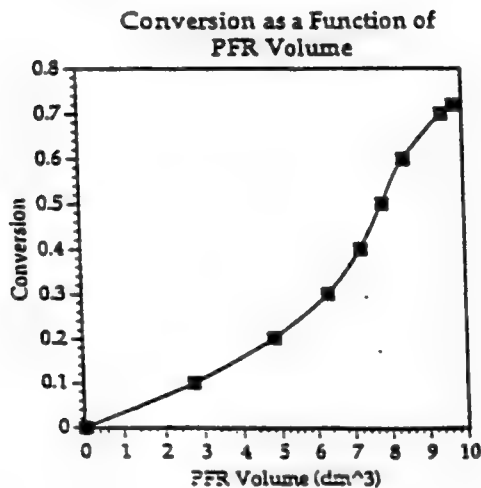
Mole Balance: $V = 7.2 = F_{Ao} \left[\int_{0.40}^{X_2} \frac{dX}{-r_A} \right] = 300 \left[\int_{0.40}^{X_2} \frac{dX}{-r_A} \right]$

At $X_2 = 0.908$, $V = 300 [\text{Area Under the curve}] = 300 [0.024] = 7.2 \text{ dm}^3$

Conversion = .908

P2-6 cont'd

(f) See plots below.



P2-7

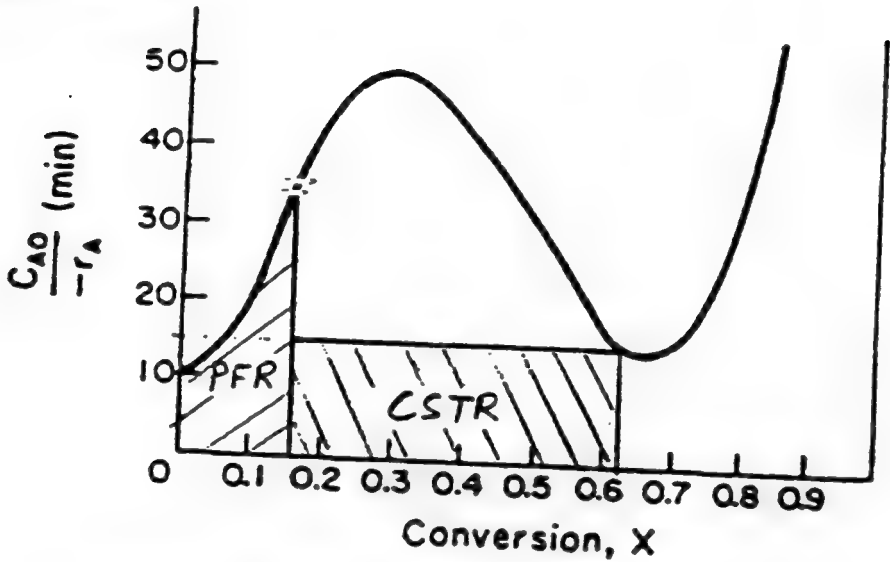
Questions from Sgt. Ambercromby:

1. Could a dent cause the stirring blade not to turn?
2. Is the temperature the same?
3. What causes the whoosh sound?
4. How much does the dent reduce the volume?

Possible reasons for the drop:

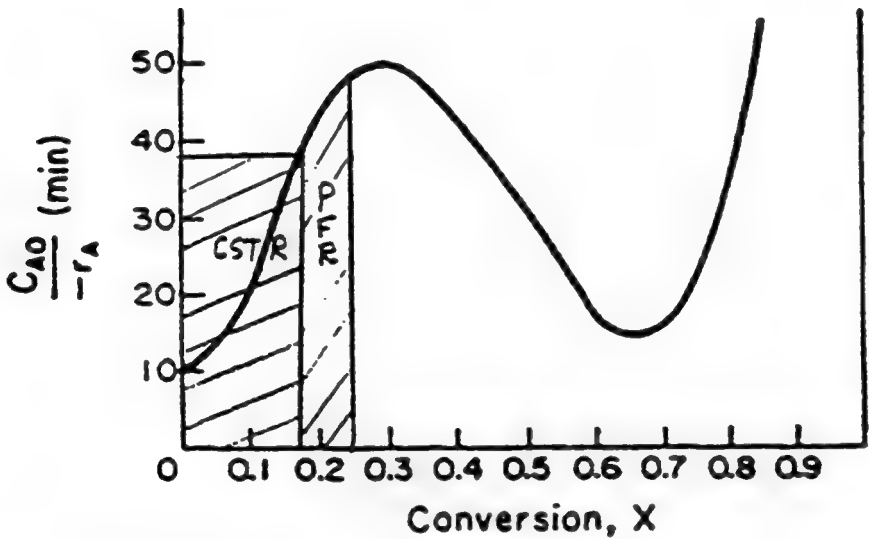
1. Temperature of the feed.
The rate of reaction depends on temperature.
2. Flow rate
Residence time depends on the flow rate. If flow rate \uparrow , residence time \downarrow , hence conversion \downarrow .
3. Level of liquid in the CSTR
If liquid level \downarrow , effective volume of CSTR \downarrow , hence conversion \downarrow .
4. Concentration of A in feed
Rate of reaction depends on the concentration of A in the feed.
5. Performance of the stirrer in the CSTR
If there is some malfunctioning in the stirrer, the CSTR will no longer be well-stirred and there will be some 'dead volume'. This decrease in the effective volume would cause a decrease in conversion.

P2-7 cont'd



Initial Operating Conditions:

$$X_0 = 0, X_1 = 0.64, X_2 = 0.82$$



Final Operating Conditions:

$$V_{\text{effective}} = 38 \times 0.17 = 6.5 \text{ dm}^3$$

$$\text{Decrease in volume} = 1.5 \text{ dm}^3$$

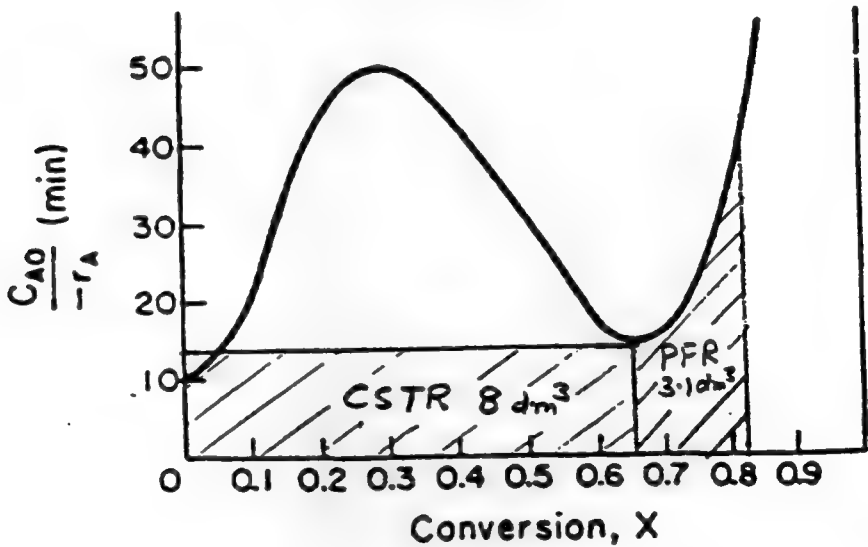
P2-7 cont'd

This 20% decrease in volume could not have been caused by a small dent. The most likely explanation is that the stirrer fell off, which caused 'dead zones' and a decrease in the effective volume.

To increase the conversion to above 0.50, switch the order of reactors. By placing the PFR before the CSTR, the necessary conversion can be achieved.

$$X_1 = 0.16$$

$$V_{\text{eff(CSTR)}} = 6.5 \text{ dm}^3 \Rightarrow X_2 = 0.62$$



P2-8.

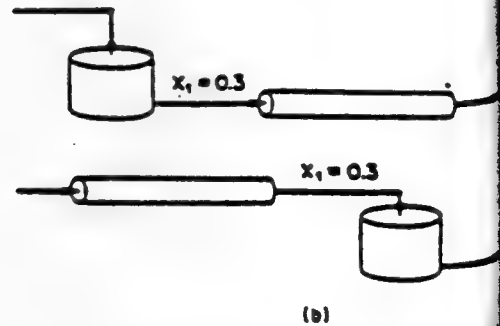
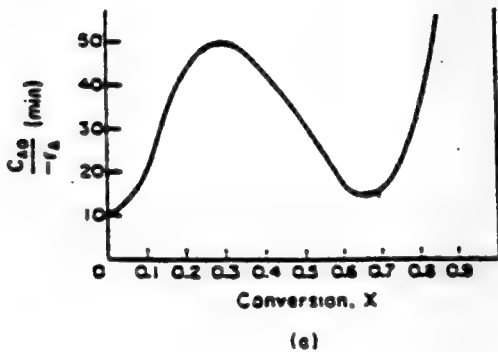


Figure P2-8.

P2-8 cont'd

a) For an intermediate conversion of 0.3, Figure P2-8a shows that a PFR yields the smallest volume, since for the PFR we use the area under the curve. A minimum volume is also achieved by following the PFR with a CSTR. In this case the area considered would be the rectangle bounded by $X=0.3$ and $X=0.7$ with a height equal to the $C_{A0}/-r_A$ value at $X=0.7$, which is less than the area under the curve.

b) $v_0 = 50 \text{ l/min}$

$$V = v_0 I, \text{ where}$$

I = area considered in part a.

$$\begin{aligned} I &= \int_0^{0.3} \frac{C_{A0}}{-r_A} dX + (0.7-0.3) \frac{C_{A0}}{-r_A} \bigg|_{X=0.7} \\ &= (0.3 - 0)(10) + \frac{1}{2} (0.3-0)(50-10) + (0.7-0.3)(15) \\ &= 15 \text{ min} \end{aligned}$$

$$\text{So } V = v_0 I = (50 \text{ l/min})(15 \text{ min}) = 750 \text{ l} = 750 \text{ dm}^3.$$

c) The smallest area can be achieved by using only one CSTR with this system.

$$I = (0.7-0) \frac{C_{A0}}{-r_A} \bigg|_{X=0.7} = (0.7-0)(15) = 10.5 \text{ min}$$

$$\text{So } V = v_0 I = (50 \text{ l/min})(10.5 \text{ min}) = 525 \text{ l}$$

We would further reduce the total volume by using a PFR at first up to the conversion that gives the same $C_{A0}/-r_A$ as $X=0.7$.

d) To obtain equal CSTR and PFR volumes the area under the curve must be equal to the area of the rectangle up to the specified conversion.

By trial and error we see that $X=0.45$ is a solution. For the CSTR,

$$I = (0.45-0) \frac{C_{A0}}{-r_A} \bigg|_{X=0.7} = (0.45-0)(37) = 16.65 \text{ min}$$

$$\text{So } V = v_0 I = (50 \text{ l/min})(16.65 \text{ min}) = 832.5 \text{ l}$$

P2-8 cont'd

For the PFR

$$I = \int_0^{0.45} \frac{C_{A0}}{-r_A} dX$$

Using Simpson's rule

$$I = \frac{0.05}{3} (10 + 4(15) + 2(20) + 4(35) + 2(43) + 4(48) + 2(50) + 4(48) + 2(43) + 37) \\ = \frac{0.05}{3} (10 + 4(15 + 35 + 48 + 48) + 2(20 + 43 + 50 + 43) + 37) = 15.72$$

$$\text{So } V = v_0 I = (50 \text{ l/min})(15.72 \text{ min}) = 786 \text{ l} \quad \text{6\% difference, pretty good}$$

There is also a solution at an $X > 0.7$

Try $X = 0.8$

For the CSTR

$$I = (0.8 - 0)(33) = 26.4 \text{ min}$$

For the PFR

$$I = \int_0^{0.8} \frac{C_{A0}}{-r_A} dX \\ = \frac{0.1}{3} (10 + 4(20) + 2(43) + 4(50) + 2(43) + 4(32) + 2(17) + 4(15) + 33) \\ = \frac{0.1}{3} (10 + 4(20 + 50 + 32 + 15) + 2(43 + 43 + 17) + 33) = 23.9 \text{ min}$$

Try $X = 0.79$

For the CSTR

$$I = (0.79)(30) = 23.7 \text{ min}$$

$$\text{So } V = v_0 I = (50 \text{ l/min})(23.7 \text{ min}) = 1185 \text{ l (dm}^3\text{)}$$

P2-8 cont'd

For the PFR

$$I = 23.9 - \frac{1}{2} (0.8 - 0.79)(30 + 33) = 23.9 - 0.315 = 23.58 \text{ min}$$

$$\text{So } V = v_0 I = (50 \text{ l/min})(23.58 \text{ min}) = 1179 \text{ l}$$

0.5% difference

$$e) \quad \tau = \frac{V}{v_0} = \frac{v_0 X \left[\frac{C_{A0}}{(-r_A)_X} \right]}{v_0} = X \frac{C_{A0}}{(-r_A)_X}$$

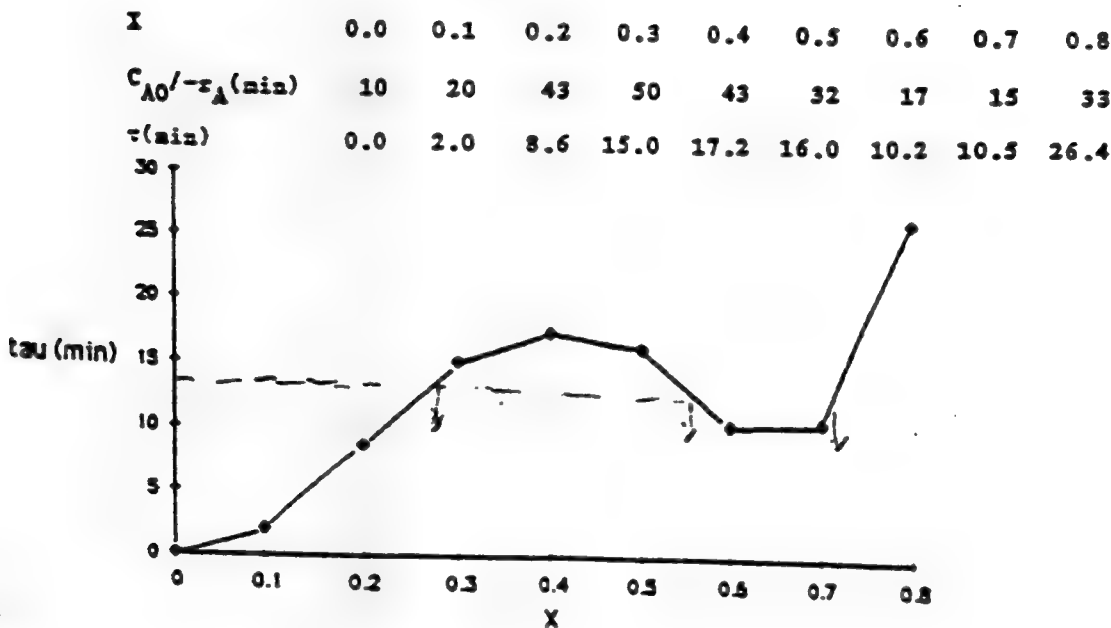


Figure P2-8E.

For our particular case

$$\tau = \frac{V}{v_0} = \frac{700 \text{ l}}{50 \text{ l/min}} = 14 \text{ min}$$

The graph yields three possible steady states

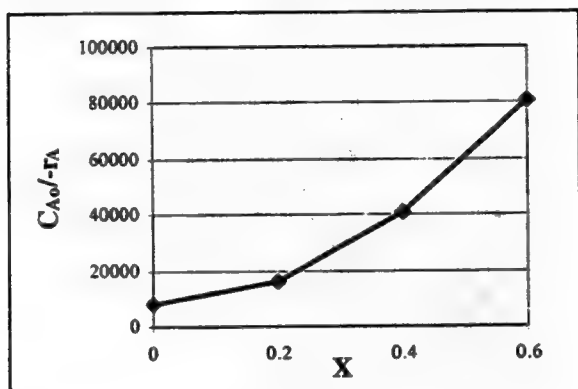
$$X_1 = 0.235, X_2 = 0.535, \text{ and } X_3 = 0.730.$$

P2-9

Data taken at 1013 kPa (10 atm) and 227°C (500.2 K)

$$y_{A0} = 0.333 \quad C_{A0} = \frac{y_{A0}P}{RT} = \frac{(0.333)(10)}{(0.082)(500.2)} = 0.08113 \text{ gmol/dm}^3$$

$-r_A$	0.000010	0.000005	0.000002	0.000001
X	0	0.2	0.4	0.6
$C_{A0}/-r_A$	8112.77	16225.54	40563.84	81127.68



(a) 30% conversion in PFR:

$$\tau_{PFR} = C_{A0} \int_0^{0.3} \frac{dX}{-r_A} = 4,664.84 \text{ s} \Rightarrow V = v_0 \tau = (4664.84 \text{ s}) \left(\frac{1 \text{ min}}{60 \text{ s}} \right) (2 \text{ m}^3/\text{min}) = 155.5 \text{ m}^3$$

(b) 30 to 50% conversion in CSTR:

$$\tau_{CSTR} = \frac{C_{A0}(X_2 - X_1)}{-r_{A2}} = 12,169.2 \text{ s} \Rightarrow V_{CSTR} = (12,169.2 \text{ s}) \left(\frac{1 \text{ min}}{60 \text{ s}} \right) (2 \text{ m}^3/\text{min}) = 405.64 \text{ m}^3$$

(c) Total Volume:

$$V_{\text{Total}} = 155.5 + 405.6 = 561.1 \text{ m}^3$$

(d) 60% conversion in PFR:

$$\tau_{PFR} = C_{A0} \int_0^{0.6} \frac{dX}{-r_A} = 20,281.9 \text{ s} \Rightarrow V_{PFR} = (20,281.9 \text{ s}) \left(\frac{1 \text{ min}}{60 \text{ s}} \right) (2 \text{ m}^3/\text{min}) = 676.06 \text{ m}^3$$

P2-9 (cont'd)

80% conversion in PFR:

r_A is not known for $X > 0.60$ – can not do.

(e) 50 % in CSTR:

$$\tau = C_{A0} \frac{X}{-r_A} = 30,422.9 \text{ s}$$

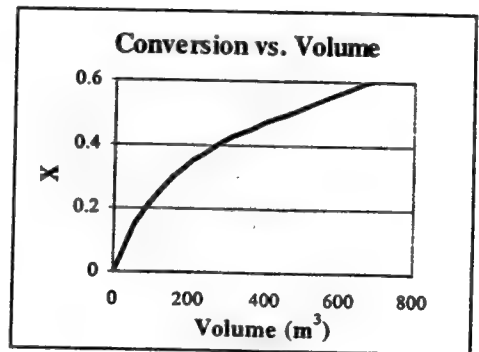
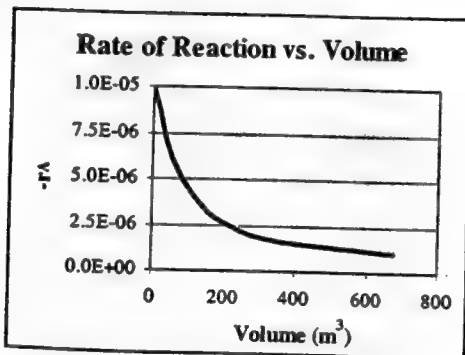
$$V = v_0 \tau = (30,422.9 \text{ s}) \left(\frac{1 \text{ min}}{60 \text{ s}} \right) (2 \text{ m}^3/\text{min}) = 1014.1 \text{ m}^3$$

(f) 50 to 60% conversion in CSTR:

$$\tau = \frac{C_{A0}(X_2 - X_1)}{-r_{A2}} = 8112.8$$

$$V = v_0 \tau = (8112.8 \text{ s}) \left(\frac{1 \text{ min}}{60 \text{ s}} \right) (2 \text{ m}^3/\text{min}) = 270.4 \text{ m}^3$$

(g)



(h) Critique

Answers are Valid:

1. Constant Temperature and Pressure
No heat effects
No pressure drop
2. Single interpolation to $X_A = 0.15, 0.30, 0.45,$ and 0.50 allowable
3. Huge volume (the size of the LA Basin)! Raise T? Raise P?

P2-10

Problem 2-10 involves estimating the volume of three reactors from a picture. The door on the side of the building was used as a reference. It was assumed to be 8 ft high.

The following estimates were made:

CSTR

$$h = 56 \text{ ft}$$

$$d = 9 \text{ ft}$$

$$V = \pi r^2 h = \pi (4.5 \text{ ft})^2 (56 \text{ ft}) = 3562 \text{ ft}^3 = 100,865 \text{ L}$$

PFR

$$\text{Length of one segment} = 23 \text{ ft}$$

$$\text{Length of entire reactor} = (23 \text{ ft}) (12) (11) = 3036 \text{ ft}$$

$$D = 1 \text{ ft}$$

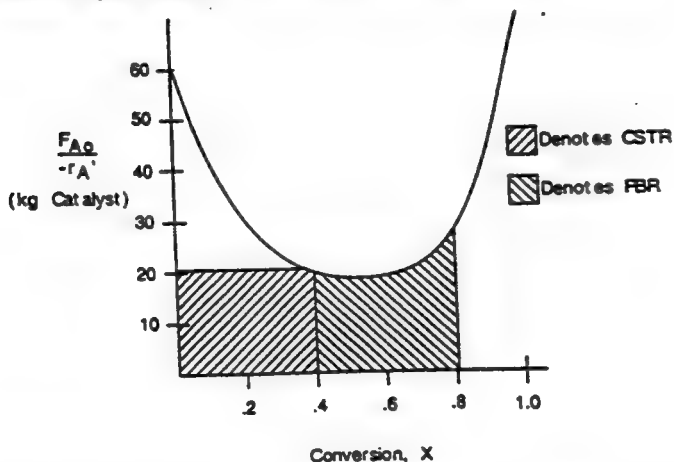
$$V = \pi r^2 L = \pi (0.5 \text{ ft})^2 (3036 \text{ ft}) = 2384 \text{ ft}^3 = 67,507 \text{ L}$$

Answers will vary for each individual.

P2-11 No solution necessary.

P2-12

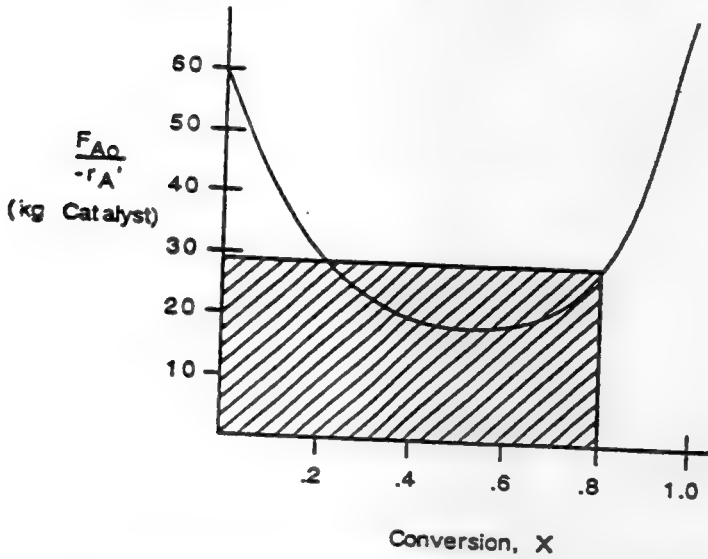
- (a) The smallest amount of catalyst necessary to achieve 80% conversion in a CSTR and PBR connected in series and containing equal amounts of catalyst can be calculated from the figure below.



The first shaded area with the lines going up from the right to the left denotes the CSTR while the area with the lines going up from right to left denotes the PBR. This figure shows that the smallest amount of catalyst used is obtained when the CSTR is used before the PBR.

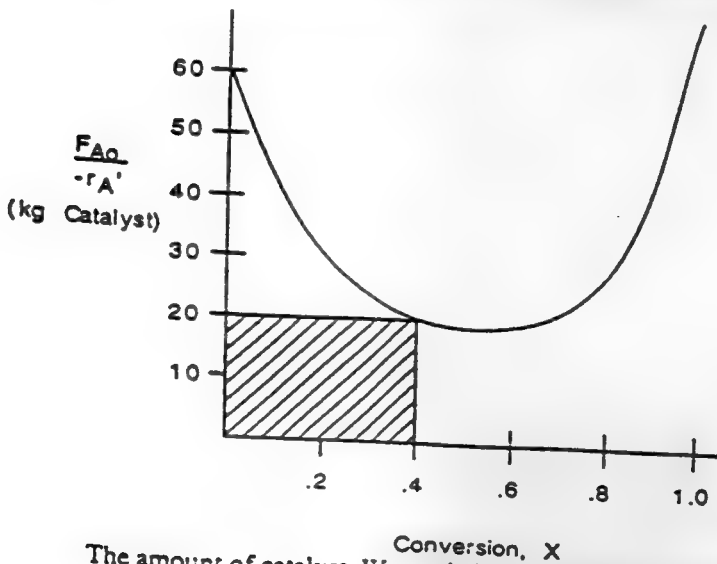
P2-12 cont'd

- (b) One can calculate the amount of catalyst needed to carry out the same reaction to 80% conversion using a single CSTR by determining the area of the shaded rectangle below.



The area of rectangle can be found to equal approximately 22.4 kg catalyst.

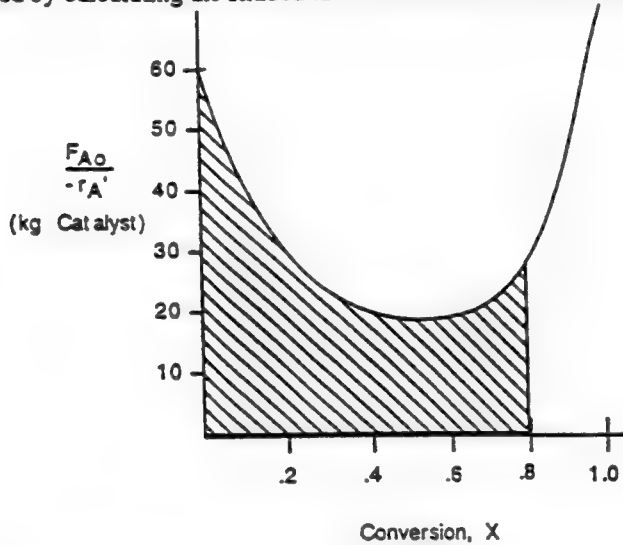
- (c) The CSTR catalyst weight necessary to achieve 40% conversion can be obtained by calculating the area of the rectangle shown in the shaded area on the figure below.



The amount of catalyst, W , needed can be found to be about 8 kg.

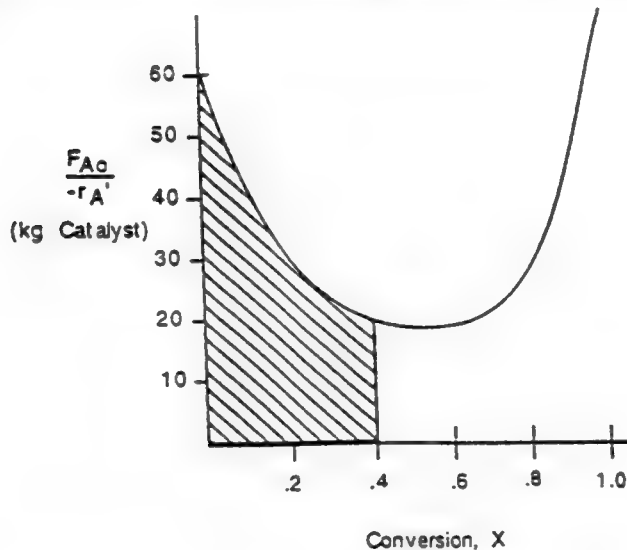
P2-12 cont'd

- (d) The catalyst weight necessary to achieve 80% conversion for a PBR can be determined by calculating the shaded area underneath the curve in the figure below



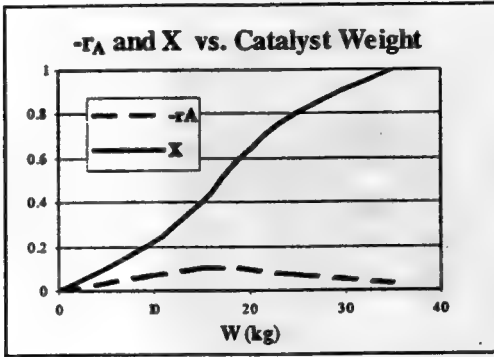
The necessary catalyst weight can be found to be approximately 30 kg.

- (e) The amount of catalyst necessary for a single PBR to obtain 40% conversion can be calculated by finding the area of the shaded region below.



The area of this region can be found to equal approximately 15 kg catalyst.

(f)



- (g) For different $(-r_A)$ vs. (X) curves, reactors should be arranged so that the smallest amount of catalyst is needed to give the maximum conversion. This can be done by minimizing the area that is occupied by a given reactor.

One useful heuristic is that for curves with a negative slope, it is generally better to use a CSTR. Similarly, when the curve has a positive slope, it is generally better to use a PBR.

P2-13 No solution will be given.

P2-14 No solution will be given.

P2-15 No solution will be given.

CDP2-A

The reaction $A \rightarrow 2 B$

$$C_{A0} = 0.2 \text{ g mol/l}$$

$$v_0 = 5.0 \text{ m}^3/\text{s}$$

a) Until the point where $-1/r_A$ is independent of X_A , i.e.

$$X = .5. \quad (\text{Both have same area until } X_A = .5)$$

$$\frac{10^{-8}}{-r_A} = 3.0 \frac{\text{m}^3}{\text{mol}}, \quad : \quad \frac{1}{-r_A} = 3 \times 10^8 \frac{\text{m}^3}{\text{mol}}$$

$$b) v_{\text{CSTR}} = \frac{F_{A0} X_A}{-r_A}$$

$$= \frac{C_{A0} v_0 X_A}{-r_A} = \frac{0.2 \times 5.0 \times 10^3}{-r_A} X_A = \frac{10^3 X_A}{-r_A}$$

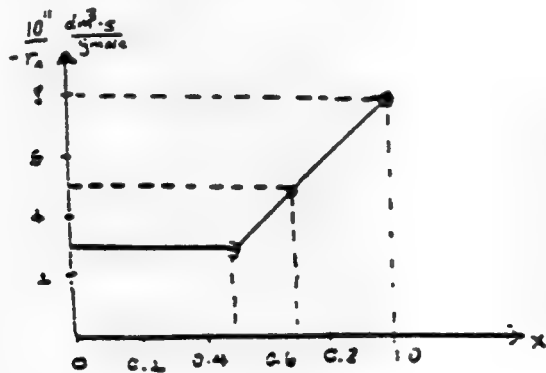
$$v_{\text{CSTR}} = 90 \text{ dm}^3$$

$$\text{assume } X_A < 0.5. \quad \text{Hence } -1/r_A = 3 \times 10^8 \frac{\text{m}^3}{\text{mol}} = 3 \times 10^{11} \frac{\text{dm}^3}{\text{mol}}$$

$$\text{so } 90 = 3 \times 10^{14} X_A$$

$$\text{and hence conversion} = X = 3 \times 10^{-13}$$

Note - our assumption was correct.



$$c) v_{\text{PFR}} = F_{A0} \int_0^{X_A} \frac{dX}{-r_A}$$

CDP2-A cont'd

$$F_{AO} = \frac{0.2 \text{ g mol}}{\text{dm}^3} \times \frac{5 \times 10^3 \text{ dm}^3}{\text{s}} = 1000 \frac{\text{g mol}}{\text{s}}$$

$$\text{so } V_{PFR} = F_A \int_0^{X_A} \frac{dX}{-r_A} = F_{AO} = 1000 \frac{\text{g mol}}{\text{s}} \int_0^{0.7} \frac{dX}{-r_A}$$

The integral on the R.H.S. using the graph is

$$= (3 \times 10^{11} \times 0.5) + \left(\frac{3 \times 10^{11} + 5 \times 10^{11}}{2} \right) \times (0.7 - 0.5) = 2.3 \times 10^{11} \frac{\text{dm}^3 \cdot \text{s}}{\text{g mol}}$$

So the plug flow reactor volume = $2.3 \times 10^{11} \text{ m}^3$ (Size of L.A. Basin).

$$\text{d) } V_{CSTR} = \frac{F_{AO}(X_2 - X_1)}{-r_A}$$

$$F_{AO} = 1000 \text{ mole/min}$$

$$X_1 = 0.70$$

$$X_2 = 0.90$$

$$-1/r_A = (\text{reaction rate})^{-1} \text{ at } X = X_2 = 7 \times 10^{11} \frac{\text{dm}^3}{\text{g mole}}$$

$$\text{so } V_{CSTR} = 1 \times (0.9 - 0.7) \times 7 \times 10^{11} \\ = 1.4 \times 10^{11} \text{ m}^3 \text{ (Size of L.A. Basin)}.$$

e) For a batch reactor

$$t = N_{AO} \int_0^X \frac{dX}{(-r_A)V}$$

$$\text{For constant pressure } V = V_0(1 + \epsilon X)$$

$$\epsilon = y_{AO} \delta$$

$$y_{AO} = 1 \text{ (pure A feed)}$$

$$\delta = \frac{2-1}{1} = 1$$

$$\text{so } \epsilon = 1$$

$$N_{AO} = V_0 C_{AO}$$

$$\text{so } t = C_{AO} \int_0^{0.4} dX \left(\frac{3 \times 10^{11}}{1+X} \right)$$

CDP2-A cont'd

$$= 0.2 \int_0^{0.4} dX \left(\frac{3 \times 10^{11}}{1+X} \right)$$

Since for X between 0 and .4, $-1/r_A$ is constant with a value
 $= 3 \times 10^{11} \text{ l/gmole}$

$$\text{So } \tau = 0.2(3 \times 10^{11}) \int_0^{0.4} \frac{dX}{1+X} = 6 \cdot 10^{10} \ln(1+X) \Big|_0^{0.4} = 6 \times 10^{10} [\ln(1.4) - \ln 1] \\ = 2.02 \times 10^{10} \text{ s}$$

= 640 yrs A reaction whose progress can be followed by generations!

Critique: This is a ridiculously small rate of reaction.

CDP2-B No solution will be given.

CDP2-C

For the CSTR:

$$V_1 = \frac{F_{A0} X_1}{-r_A} = F_{A0} (\text{Area})$$

$$\text{Area} = \frac{V_1}{F_{A0}} = \frac{1200 \text{ ft}^3}{5 \text{ lbmol/hr}} = 240$$

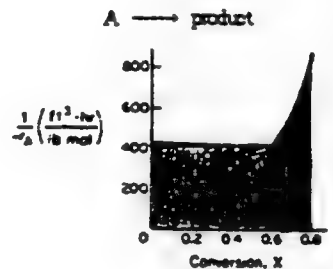
From the graph we can see that $X_1 = 0.60$

For the PFR:

$$V_2 = \frac{F_{A0} (X_2 - X_1)}{-r_A} = F_{A0} (\text{Area under curve})$$

$$\text{Area under curve} = \frac{V_2}{F_{A0}} = \frac{600}{5} = 120$$

From the graph we can see that $X_2 = 0.80$



CDP2-D

400 L CSTR and 100 L PFR

Feed is 41% A, 41% B, and 18% I.

$P = 10 \text{ atm}$ $T = 227^\circ\text{C} = 500 \text{ K}$

$$C_{T0} = \frac{P}{RT} = \frac{10 \text{ atm}}{(0.082 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(500 \text{ K})} = 0.244 \text{ mol/L}$$

$$C_{A0} = 0.41 C_{T0} = 0.41(0.244 \text{ mol/L}) = 0.1 \text{ mol/L}$$

$$F_{A0} = v_0 C_{A0} = 1 \text{ L/s}(0.1 \text{ mol/L}) = 0.1 \text{ mol/s} = 6 \text{ mol/min}$$

(a) There are two possible arrangements of the system:

1. CSTR followed by the PFR

2. PFR followed by the CSTR

Case 1: CSTR \rightarrow PFR

$$\text{CSTR: } V_1 = F_{A0}(\text{Area})$$

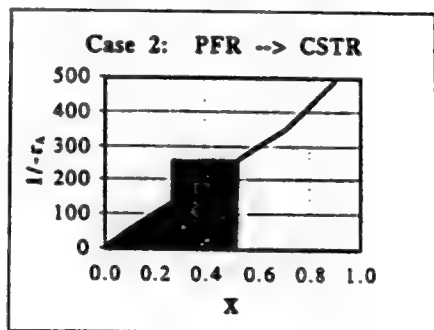
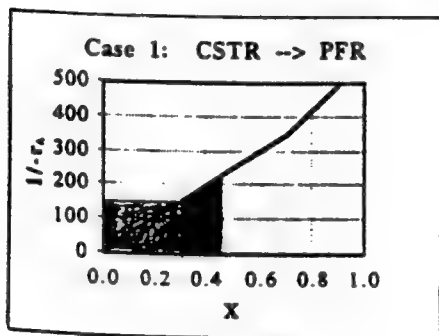
$$\text{Area} = \frac{V_1}{F_{A0}} = \frac{400}{6} = 66.67$$

From the graph - $X_1 = 0.36$

$$\text{PFR: } V_2 = F_{A0}(\text{Area under curve})$$

$$\text{Area under curve} = \frac{V_2}{F_{A0}} = \frac{100}{6} = 16.667$$

From the graph - $X_2 = 0.445$



Case 2: PFR \rightarrow CSTR

PFR: Area under curve = 16.67

From the graph - $X_1 = 0.259$

CSTR: Area = 66.67

From the graph - $X_2 = 0.515$

2.27

- (b) Two 400 L CSTR's in series.

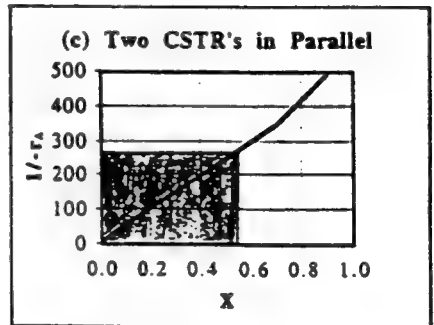
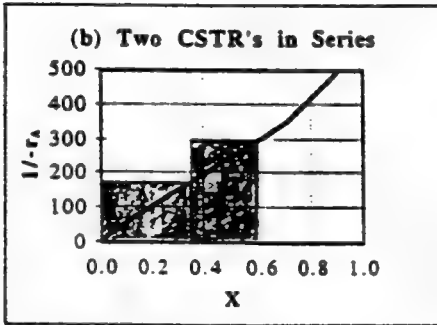
$$\text{CSTR1: } V = F_{A0}(\text{Area})$$

$$\text{Area} = 66.67$$

$$\text{From the graph} - X_1 = 0.36$$

$$\text{CSTR2: } \text{Area} = 66.67$$

$$\text{From the graph} - X_2 = 0.595$$



- (c) Two 400 L CSTR's in parallel.

To each CSTR goes half of the feed.

$$F_{A0} = 6/2 = 3 \text{ mol/min}$$

$$V = F_{A0}(\text{Area})$$

$$\text{Area} = \frac{V}{F_{A0}} = \frac{400}{3} = 133.3$$

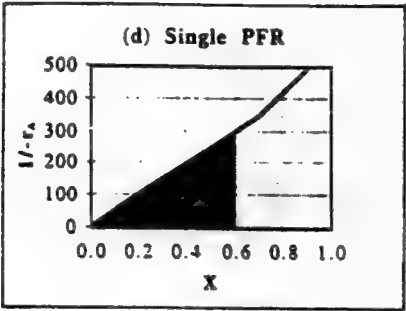
$$\text{From the graph: } X = 0.52$$

- (d) PFR: $V = F_{A0}(\text{Area under curve})$

From the graph we can find the area under the curve for a conversion of 0.60:

$$\text{Area} = \frac{(0.60)(300)}{2} = 90$$

$$V = (2 \text{ mol/min})(90) = 180 \text{ L}$$



(e) Pressure reduced by a factor of 10.

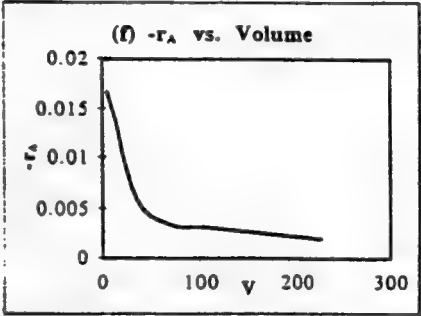
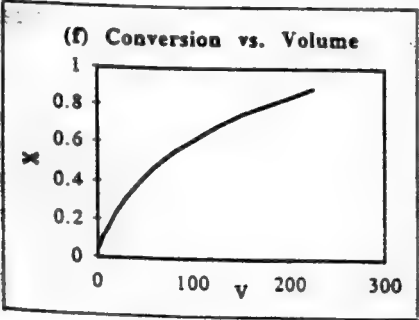
A decrease in pressure would cause a decrease in the overall concentration which would in turn cause a decrease in C_{A0} and F_{A0} . By looking at the design equation:

$$V = \frac{F_{A0} X}{-r_A}$$

it is apparent that to compensate for the decrease in F_{A0} there would be an increase in X .

(f) Use the graph of $1/-r_A$ vs. X to find values for all volumes. (Assume a flow rate of 1 mol/min.) Generate the following table and graphs:

X	$-r_A$	V
0	0.2	0
0.1	0.0167	3.494
0.4	0.00488	42.984
0.7	0.00286	125.878
0.9	0.00204	225.088



Chapter 3

P3-1. See P4-1, page 205 of the text for guidelines.

P3-2. (c), the point is that the rate law (Eqn. E3-2.1) is not valid at very low concentrations of NaOH (i.e. the rate law predicts a rate of reaction even if $C_{\text{NaOH}} \equiv 0$).

P3-3. This problem motivates the students as they see applications of CRE outside examples found in chemical plants. Surprisingly, the activation energies are essentially the same.

P3-4. Short problem from DuPont about competing effects corrosion rate as a function of concentration and temperature that involves reasoning, no calculations.

P3-5. Challenges the rule of thumb, the rate doubles for every 10°C increase in temperature, that the students learned in chemistry. Part (b) is a dull version of P3-3.

P3-6. Short problem that reinforces the specific reaction rate, k_i , must be defined w.r.t. a particular species i . This problem, which helps lay the foundation for multiple reactions in chapter 6, can be given at the same time as P3-10.

Problems P3-7, P3-8, P3-9, P3-11, P3-12, and P3-13 all give practice at setting up stoichiometric tables. The industrial flow sheets are given for P3-8 and P3-11. These problems can be alternately assigned from year to year. My favorite is P3-7.

P3-9. This problem begins to prepare the students for those situations (e.g. membrane reactors, multiple reactions) where they cannot use conversion as a variable.

P3-10. This problem reinforces the concept that at or near equilibrium, the rate law must reduce to give the equilibrium conversion (and the concentrations) that are derived from thermodynamics.

P3-11. See above.

P3-12. See above.

P3-13. See above.

P3-14. Reinforces the point that the equilibrium conversion will be different for a flow system and a constant volume batch system.

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- P3-15.** Uses the rate law and stoichiometric table to give practice at expressing $-r_A=f(X)$. In Chapter 2 the student saw that once one has $-r_A=f(X)$ a number of reaction systems can be designed.
- P3-16.** Straight forward problem to set up a stoichiometric table and then substitute numbers to calculate various parameters.
- P3-17.** Alternate to P3-14.
- P3-18.** This problem to express $-r_A=f(X)$ requires thinking and is not particularly straight forward. Reinforces the fact that concentration must be known as a function of pressure. Prepares the student for pressure drop problems in chapter 4.
- P3-19.** Requires the student to go outside of the textbook for information and practice life-long learning skills.
- P3-20.** Usually assigned at graduate level in conjunction with Appendices I and J.

Problems P3-21, P3-22, and P3-23 all involve setting up stoichiometric tables for reactions with phase changes.

- CDP3-A** Similar to the honey bee, firefly, and cricket problem where the activation energy must be calculated.
- CDP3-B** Similar to problem P3-23.
- CDP3-C** Points out that the concentration of B in the gas phase can be a constant.
- CDP3-D** Alternative to problem P3-22.
- CDP3-E** Alternative to problem P3-12.

Summary

	<u>Assigned</u>	<u>Alternates</u>	<u>Difficulty</u>	<u>Time</u>	<u>Solution Given</u>
P3-1	S				No
P3-2	O				(b&c) Yes
P3-3	O	A	FSF	40	Yes
● P3-4			SF	15	Yes
● P3-5	I		SF	30	Yes
● P3-6		7,8,11,12,B,E		20	Yes
● P3-7		7,8,11,12,13,E		65	Yes
● P3-8	AA	7,11,12,13,E		35	No
● P3-9	A(a&b)			20&20	Yes
● P3-10				20	Yes

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P3-11	AA	7,8,11,12,13,E	45	Yes
P3-12	AA	7,8,11,12,13,E	35	Yes
P3-13	AA	7,8,11,12,13,E	35	Yes
● P3-14	AA	17	45	Yes
P3-15	O	13	35	Yes
P3-16	O		45	Yes
● P3-17	AA	14	30	Yes
● P3-18	A		50	Yes
P3-19	G		60	No
P3-20	G		45	No
P3-21	G	22,C,D	50	Yes
P3-22	G	21,C,D	50	Yes
P3-23	G	B	50	Yes
CDP3-A	AA	3	15	Yes
CDP3-B	AA	23	30	Yes
CDP3-C	AA		45	Yes
CDP3-D	AA	C,21,22	30	Yes
CDP3-E	AA	7,8,11,12,13	25	Yes

Assigned

● = Always assigned, AA = Always assign one from the group of alternates,
O = Often, I = Infrequently, S = Seldom, G = Graduate level

Alternates

In problems that have a dot in conjunction with AA means that one of the problems, either the problem with a dot or any one of the alternates are always assigned.

Time

Approximate time in minutes it would take a B/B* student to solve the problem.

Difficulty

SF = Straight forward reinforcement of principles (plug and chug)

FSF = Fairly straight forward (requires some manipulation of equations or an intermediate calculation).

IC = Intermediate calculation required

M = More difficult

OE = Some parts open-ended.

Note the letter problems are found on the CD-ROM. For example A = CDP1-A.

Summary Table Ch-3

	Arrhenius Equation	Rate Law	Equilibrium	Stoichiometry	Rate Law & Stoichiometry	Phase Change
	3,5,19,A	6,10	14,17	Gas 7(b)&(c),11, 12,13,E Liquid 7(a)	9(b)&(c), 13(d),16(c), 9(a)	21,22,23, B,C
Straight Forward		6,10(a)		7,12	16(c),E	21
Fairly Straight Forward	3(a)		14,17	11,13	9,13(d)	22,D,C
More Difficult	3(b)	10(b),10(c)				23,B
Open-ended	3(c)			11(e)		
Critical Thinking	3(d)					

Chapter 3

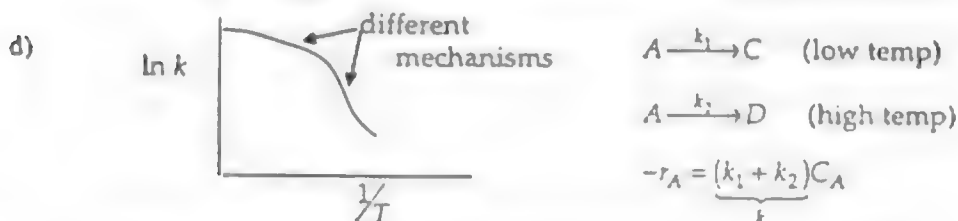
P3-1 No solution will be given

P3-2

a) Cooking food (effect of temperature), removing a stain with bleach (effect of bleach concentration), dissolution of sugar in tea or coffee.

b) Parts a and b will stay the same while the reaction rates will increase by a factor of ten.

c) Rate law should always be determined from an experimental observation
 $-r_A = kC_{\text{NaOH}}$ the reaction rate is zero-order with respect to NaOH.



e) Cake will burn on the outside because the cake dough offers a resistance to heat transfer so reaction temperature will be lower in the center of the cake than on the outside.

P3-3 Given: Frequency of flashing of fireflies and the frequency of chirping of crickets as a function of temperature:

A. Fireflies

T°C	21.0	25.0	30.0
Flashes/min.	9.0	12.16	16.2
T°K	294	298	303
1/T°K×1000	3.401	3.356	3.300

B. Crickets

T°C	14.2	20.3	27.0
Chirps/min.	80	126	200
T°K	287.2	293.3	300°K
1/T°K×1000	3.482	3.409	3.333

P3-3 cont'd

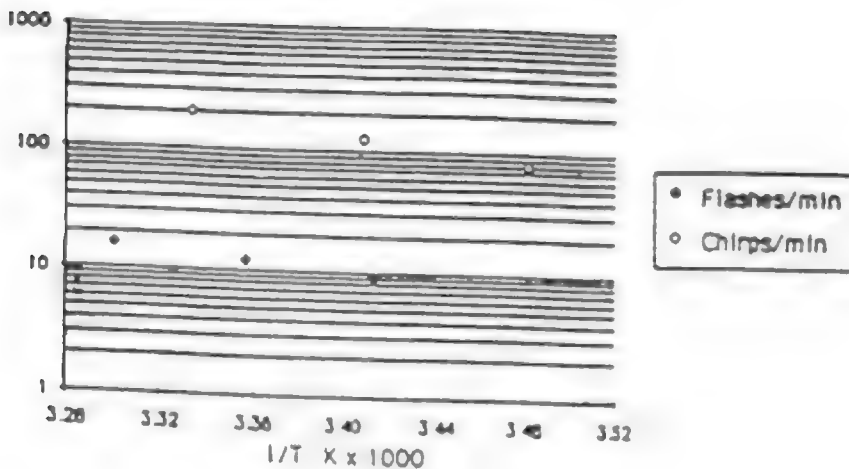


Figure P3-2.

Assume an Arrhenius dependence for both the flashing rate and the chirp rate.

i.e.

$$r_F = A_F e^{-E_F/RT} = \text{flashing rate}$$

$$r_C = A_C e^{-E_C/RT} = \text{chirping rate}$$

Then:

$$\ln r_F = \ln A_F - E_F/RT \text{ and}$$

b) Flight Speed of the Honey bee

T(C)	1/T(K)	V(cm/s)	ln(V)
25	3.3557	0.7	-0.356675
30	3.30033	1.8	0.587787
35	3.24675	3	1.098612

From the graph:

$$E = 13.4 \text{ kcal/mole}$$

Therefore at 40°C,

$$\ln(V) = -13.378(3.73) + 44.603 = 1.86$$

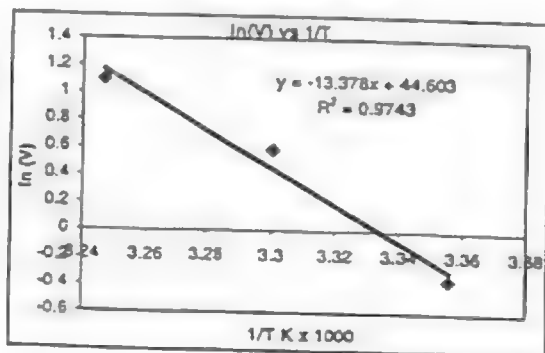
$$V = 6.44 \text{ cm/s}$$

At -5°C,

$$\ln(V) = -13.378(3.73) + 44.603 = -5.31$$

$$V = 0.005 \text{ cm/s}$$

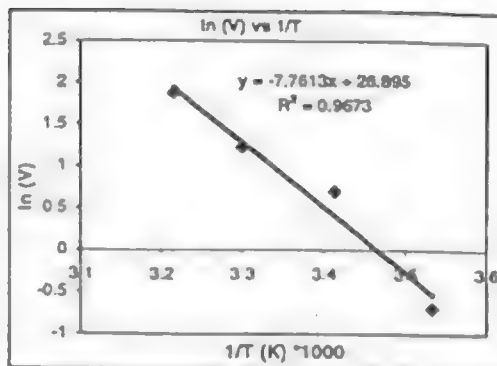
Unfortunately for the bee, it would not be alive at this temperature.



P3-3 cont'd

Running Speed of Ants

T	1/T (K)	V	ln (V)
10	3.53357	0.2	-0.693147
20	3.41297	2	0.693147
30	3.30033	3.4	1.223775
40	3.21543	6.5	1.871802



From the graph:

$$E = -7.7613 \text{ kcal/mole}$$

- c) The activity of bees, ants, crickets, and fireflies increases with an increase in temperature. The activation energy of fireflies and crickets is the same while ants and bees have a different frequency that is dependent on temperature.
- d) There is a limit to the temperature for which the data for any one of the insects can be extrapolated. Data which would be helpful is the maximum and the minimum temperature that these insects can endure before death. Therefore, even if extrapolation gives us a value that looks reasonable, at certain temperatures it could be useless.

P3-4. There are two competing effects that bring about the maximum in the corrosion rate: temperature and HCN-H₂SO₄ complex concentration. The corrosion rate increases with increasing temperature and increasing concentration of the HCN-H₂SO₄ complex. The temperature increases as we go from the top to bottom of the column, and consequently the rate of corrosion should increase. However, the HCN concentration (and the HCN-H₂SO₄ complex) decreases as we go from the top to the bottom of the column. There is virtually no HCN in the bottom of the column. These two opposing factors result in a maximum in the corrosion rate somewhere around the middle of the column.

P3-5. If a reaction rate doubles for an increase in 10°C, at $T = T_1$ let $k = k_1$ and at $T = T_2 = T_1 + 10$, let $k = k_2 = 2k_1$; then with $k = Ae^{-E/RT}$ in general, $k_1 = Ae^{-E/RT_1}$ and $k_2 = Ae^{-E/RT_2}$, or

$$\frac{k_2}{k_1} = e^{-E/R(\frac{1}{T_2} - \frac{1}{T_1})} \text{ or } \frac{E}{R} = -\frac{\ln k_2/k_1}{(1/T_2 - 1/T_1)} = -\frac{\ln k_2/k_1}{(T_1 - T_2)/T_1 T_2}$$

P3-5 cont'd

$$\therefore E = R \frac{\ln(k_2/k_1)(T_1(T_1 + 10))}{(T_2 - T_1)} = \frac{R \ln 2 (T_1(T_1 + 10))}{10^\circ\text{K}}$$

$$T_1(T_1 + 10) = \frac{(10)^\circ\text{K} E}{R \ln 2}$$

$$\text{which can be approximated by } T = \left(\frac{(10)^\circ\text{K} E}{R \ln 2} \right)^{1/2}$$

7b) Given the following data

$$k \text{ min}^{-1} \quad .001 \quad 0.050$$

$$T^\circ\text{C} \quad 0 \quad 100$$

$$\text{Then } T^\circ\text{K} \quad 273 \quad 373$$

$$\text{Eqn. 3-2 is } k = A e^{-E/RT}$$

$$\text{Then at } T_1 = 0^\circ\text{C}, k_1 = A e^{-E/RT_1}, \text{ and at } T_2 = 100^\circ\text{C}, k_2 = A e^{-E/RT_2}$$

$$\text{Dividing } \frac{k_2}{k_1} = e^{-E/R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\text{or } E = - \frac{R \ln(k_2/k_1)}{(1/T_2 - 1/T_1)} = \frac{R T_1 T_2}{(T_2 - T_1)} \ln(k_2/k_1)$$

$$\therefore E = \frac{[1.99 \text{ cal/mol}^\circ\text{K}][273^\circ\text{K}][373^\circ\text{K}]}{100^\circ\text{K}} \ln\left(\frac{.050}{.001}\right) = 7,960 \text{ cal/mol} \quad \text{and}$$

$$\therefore A = k_1 e^{+E/RT_1} = 10^{-3} \exp \left[\frac{7960 \text{ cal/mol}}{1.99 \text{ cal/mol}^\circ\text{K} \times 273^\circ\text{K}} \right] \text{min}^{-1} = 2.1 \times 10^3 \text{ min}^{-1} \quad \text{and}$$

P3-6 Solution

For this problem, recall that for any reaction



the rate laws are related to the stoichiometric coefficients by the following equation.

P3-6 cont'd

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

$$(a) \quad -r_B = \frac{b}{a}(-r_A) = \frac{1}{2}(k_A C_A^2 C_B)$$

$$-r_B = k_B C_A^2 C_B \quad \text{where} \quad k_B = 12.5 \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 \left(\frac{1}{\text{sec}} \right)$$

$$r_C = \frac{c}{a}(-r_A) = \frac{1}{2}(k_A C_A^2 C_B)$$

$$r_C = k_C C_A^2 C_B \quad \text{where} \quad k_C = 12.5 \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 \left(\frac{1}{\text{sec}} \right)$$

$$(b) \quad -r_B = \frac{b}{a}(-r_A) = 3(k_A C_A C_B)$$

$$-r_B = k_B C_A C_B \quad \text{where} \quad k_B = 75.0 \left(\frac{\text{dm}^3}{\text{mol sec}} \right)$$

$$r_C = \frac{c}{a}(-r_A) = 2(k_A C_A C_B)$$

$$r_C = k_C C_A C_B \quad \text{where} \quad k_C = 50.0 \left(\frac{\text{dm}^3}{\text{mol sec}} \right)$$

$$(c) \quad r_B = \frac{b}{a}(-r_A) = 3 \left[k_A \left(C_A^2 - \frac{C_B^4}{K_C} \right) \right]$$

$$r_B = k_B \left[C_A^2 - \frac{C_B^4}{K_C} \right] \quad \text{where} \quad k_B = 75.0 \left(\frac{\text{dm}^3}{\text{mol sec}} \right)$$

$$(d) \quad -r_B = \frac{b}{a}(-r_A) = \frac{5}{4}(k_A C_A^2 C_B)$$

$$-r_B = k_B C_A^2 C_B \quad \text{where} \quad k_B = 31.25 \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 \left(\frac{1}{\text{sec}} \right)$$

$$r_C = \frac{c}{a}(-r_A) = (k_A C_A^2 C_B)$$

P3-6 cont'd

$$r_c = k_c C_A^2 C_B \quad \text{where} \quad k_c = 25.0 \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 \left(\frac{1}{\text{sec}} \right)$$

$$r_D = \frac{d}{2} (-r_A) = \frac{3}{2} (k_A C_A^2 C_B)$$

$$r_D = k_D C_A^2 C_B \quad \text{where} \quad k_D = 37.5 \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 \left(\frac{1}{\text{sec}} \right)$$

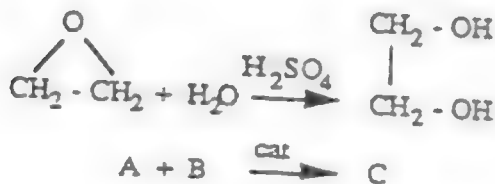


Reactions are related by $\frac{-r_{\text{CH}_4}}{1} = -2/3 r_{\text{O}_2} = r_{\text{HCOOH}} = r_{\text{H}_2\text{O}}$
or

$$r_{\text{CH}_4} = 2/3 r_{\text{O}_2} \quad \underline{C.}$$

P3-7

a)



Because this is a liquid phase reaction, the stoichiometric table will be the same whether the reaction is carried out in either a batch or flow reactor.
 $N_A/V = N_A/V_0 = C_A$

Species	Symbol	Initial	Change	Remain
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH}_2 \end{array}$	A	$C_{A0} = 1 \text{ lb mol/ft}^3$	$-C_{A0}X$	$C_A = 1(1-X)$
H_2O	B	$C_{B0} = 3.47 \text{ lb mol/ft}^3$ $\theta_B = 3.47$	$-C_{A0}X$	$C_B = (3.47-X)$
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{OH} \end{array}$	C	0	$+C_{A0}X$	$C_C = X$

P3-7 cont'd



Species	Symbol	Entering	Change	Leaving
C_2H_6	A	F_{AO}	$-F_{AO}X$	$F_A = F_{AO}(1-X)$
C_2H_4	B	0	$+F_{AO}X$	$F_B = F_{AO}X$
H_2	C	0	$+F_{AO}X$	$F_C = F_{AO}X$
		$F_{TO} = F_{AO}$		$F_T = F_{AO}(1+X)$

Gas Phase, constant temperature, and no pressure drop.

$$v = v_0(1+EX)$$

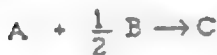
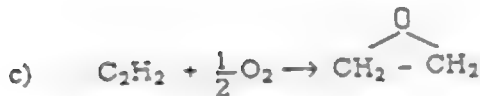
$$E = y_{AO} \delta = 1(1+1-1) = 1$$

$$v = v_0(1+X)$$

$$C_A = \frac{F_A}{v} = \frac{F_{AO}(1-X)}{v_0(1+X)} = C_{AO} \frac{(1-X)}{(1+X)}$$

$$C_B = C_C \frac{F_B}{v} = \frac{F_{AO}X}{v_0(1+X)} = C_{AO} \frac{X}{1+X}$$

$$C_{AO} = y_{AO} C_{TO} = y_{AO} \frac{P_0}{RT_0} = \frac{(1)(6 \text{ atm})}{\frac{0.082 \text{ m}^3}{\text{K} \cdot \text{mol}} \text{ atm} / 100^\circ \text{K}} = 0.067 \frac{\text{kmol}}{\text{m}^3} = 0.067 \frac{\text{mol}}{\text{dm}^3}$$



Species	Symbol	Entering	Change	Leaving
C_2H_2	A	F_{AO}	$-F_{AO}X$	$F_A = F_{AO}(1-X)$
O_2	B	F_{BO}	$-1/2 F_{AO}X$	$F_B = F_{AO}(0.5-X/2)$
Ethylene oxide	C	0	$F_{AO}X$	$F_C = F_{AO}X$

P3-7 cont'd

Gas Phase, Isothermal and no pressure drop.

$$\theta_s = \frac{\frac{1}{2} F_{A0}}{F_{A0}} = \frac{1}{2}$$

$$y_{A0} = \frac{F_{A0}}{F_{T0}} + \frac{1}{1 + \theta_s} = \frac{1}{1 + 0.5} = .67$$

$$\varepsilon = y_{A0} \delta = 0.67 \left(1 - \frac{1}{2} - 1 \right) = -0.34$$

$$C_{A0} = y_{A0} C_{T0} = y_{A0} \frac{P_0}{RT_0} = 0.67 \frac{6 \text{ atm}}{\left(\frac{0.082 \text{ atm dm}^3}{\text{mol K}} \right) (533 \text{ K})}$$

$$C_{A0} = 0.092 \frac{\text{mol}}{\text{dm}^3}$$

$$C_A = \frac{F_{A0}}{v} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = C_{A0} \frac{(1-X)}{1+\varepsilon X} = \frac{(0.092)(1-X)}{1-0.34X}$$

$$C_s = C_{A0} \frac{\left(\theta_s - \frac{X}{2} \right)}{1+\varepsilon X} = \frac{0.092 \left(\frac{1}{2} - \frac{1}{2} X \right)}{1-0.15X} = \frac{0.046(1-X)}{1-0.34X}$$

$$C_C = \frac{C_{A0} X}{1+\varepsilon X} = \frac{0.092 X}{1-0.34X}$$

P3-8

An inert, Nitrogen would be added to the stoichiometry table

Species	Symbol	Entering	Change	Leaving
C_2H_4	A	F_{A0}	$-F_{A0}X$	$F_{A0} = -F_{A0}(1-X)$
O_2	B	$F_{B0} = \theta_B$	$-1/2 F_{A0}X$	$F_B = F_{A0}(\theta_B - X/2)$
N_2	I	$F_I = \theta_I F_{A0}$	—	$F_I = F_{A0} \theta_I$
Ethylene oxide	C	0	$F_{A0}X$	$F_C = F_{A0}X$

Gas Phase, Isothermal, and no Pressure drop

$$\theta_s = \frac{\frac{1}{2} F_{A0}}{F_{A0}} = \frac{1}{2}$$

P3-8 cont'd

$$\theta_1 = \theta_s \frac{.79}{.21} = \left(\frac{1}{2} \right) \left(\frac{.79}{.21} \right) = 1.88$$

$$y_{A0} = \frac{F_{A0}}{F_{T0}} = \frac{1}{1 + \theta_1 + \theta_s} = \frac{1}{1 + 0.5 + 1.88} = 0.30$$

$$\epsilon = y_{A0} \delta = 0.30 \left(1 - \frac{1}{2} - 1 \right) = -0.15$$

The inert Nitrogen would also change the values of y_{A0} and ϵ .

P3-9



Mole Balance for a CSTR:

$$F_{A0} - F_A = -r_A V$$

$$F_{B0} - F_B = -r_B V$$

$$F_{C0} - F_C = -r_C V$$

Rate Law:

$$-r_A = k C_A C_B$$

Stoichiometry:

$$-r_A = -r_B = r_C$$

Combine with Eq 3-40 and 3-48: Liquid phase

$$F_{A0} - F_A = k \left(\frac{F_{T0}}{V_0} \right)^2 \left(\frac{F_A}{F_A + F_B + F_C} \right) \left(\frac{F_B}{F_A + F_B + F_C} \right) V$$

$$F_{B0} - F_B = k \left(\frac{F_{T0}}{V_0} \right)^2 \left(\frac{F_A}{F_A + F_B + F_C} \right) \left(\frac{F_B}{F_A + F_B + F_C} \right) V$$

$$F_{C0} - F_C = k \left(\frac{F_{T0}}{V_0} \right)^2 \left(\frac{F_A}{F_A + F_B + F_C} \right) \left(\frac{F_B}{F_A + F_B + F_C} \right) V$$

P3-9 cont'd

(b) $A+B \rightarrow C$

Mole balance for a PFR:

$$\frac{dF_A}{dV} = -r_A$$

$$\frac{dF_B}{dV} = -r_B$$

$$\frac{dF_C}{dV} = -r_C$$

Rate Law:

$$-r_A = kC_A C_B$$

Stoichiometry:

$$-r_A = -r_B = r_C$$

Combine with Eq. 3-40 and 3-48:

$$\frac{dF_A}{dV} = k \left(\frac{F_{T0}}{v_0} \right)^2 \left(\frac{F_A}{F_A + F_B + F_C} \right) \left(\frac{F_B}{F_A + F_B + F_C} \right)$$

$$\frac{dF_B}{dV} = k \left(\frac{F_{T0}}{v_0} \right)^2 \left(\frac{F_A}{F_A + F_B + F_C} \right) \left(\frac{F_B}{F_A + F_B + F_C} \right)$$

$$\frac{dF_C}{dV} = -k \left(\frac{F_{T0}}{v_0} \right)^2 \left(\frac{F_A}{F_A + F_B + F_C} \right) \left(\frac{F_B}{F_A + F_B + F_C} \right)$$

This set of differential equations can be solved using POLYMATH or a similar software package.

(c) $A \rightarrow B+C$ (gas phase reaction)

Mole Balance for a PFR:

$$\frac{dF_A}{dV} = -r_A$$

$$\frac{dF_B}{dV} = -r_B$$

$$\frac{dF_C}{dV} = -r_C$$

Rate Law:

$$r_A = kC_A$$

Stoichiometry:

$$-r_A = r_B = r_C$$

Combine with Eq. 3-40 and 3-48:

$$\frac{dF_A}{dV} = k \frac{P_{T0}}{RT_0} \left(\frac{F_A}{F_A + F_B + F_C} \right)$$

P3-9 cont'd

$$\frac{dF_B}{dV} = -k \frac{P_{T_0}}{RT_0} \left(\frac{F_A}{F_A + F_B + F_C} \right)$$

$$\frac{dF_C}{dV} = -k \frac{P_{T_0}}{RT_0} \left(\frac{F_A}{F_A + F_B + F_C} \right)$$

This set of differential equations can be solved using POLYMATH or a similar software package.



Mole balance for a PFR:

$$\frac{dF_A}{dV} = -r_A$$

$$\frac{dF_B}{dV} = -r_B$$

$$\frac{dF_C}{dV} = -r_C$$

Rate Law:

$$-r_A = k C_A C_B^{0.5}$$

Stoichiometry:

$$-r_A = -2r_B = r_C$$

Combine with Eq. 3-40 and 3-48:

$$\frac{dF_A}{dV} = k \left(\frac{P_{T_0}}{RT_0} \right)^{\frac{3}{2}} \left(\frac{F_A}{F_A + F_B + F_C} \right) \left(\frac{F_B}{F_A + F_B + F_C} \right)^{\frac{1}{2}}$$

$$\frac{dF_B}{dV} = \frac{1}{2} k \left(\frac{P_{T_0}}{RT_0} \right)^{\frac{3}{2}} \left(\frac{F_A}{F_A + F_B + F_C} \right) \left(\frac{F_B}{F_A + F_B + F_C} \right)^{\frac{1}{2}}$$

$$\frac{dF_C}{dV} = -k \left(\frac{P_{T_0}}{RT_0} \right)^{\frac{3}{2}} \left(\frac{F_A}{F_A + F_B + F_C} \right) \left(\frac{F_B}{F_A + F_B + F_C} \right)^{\frac{1}{2}}$$

This set of differential equations can be solved using POLYMATH or a similar software package.

P3-10.

a) At high temperatures



At equilibrium, we know from thermodynamics

$$K_C = \frac{C_{B,e}}{C_{A,e}} \quad (\text{PS39.1})$$

Consequently, we know that the rate law most reduced to Equation (PS3-9.1) when $-r_A = 0$

Therefore

$$-r_A = k \left[C_A - \frac{C_B}{K_C} \right] \quad (\text{PS39.2})$$

At equilibrium $-r_A = 0$ and equation (PS3-9.2) becomes upon rearrangement

$$K_C = \frac{C_{B,e}}{C_{A,e}}$$



At low temperatures reaction is irreversible and the rate law is:

$$-r_A = k C_A^{1/2} C_B$$

$$-r_{A, \text{toward}} = k_1 C_A^{1/2} C_B, \quad -r_{A, \text{reverse}} = -k_2 C_D$$

$$-r_A = k_1 C_A^{1/2} C_B - k_2 C_D$$

$$= k_1 \left(C_A^{1/2} C_B - \frac{k_2}{k_1} C_D \right)$$

$$= k_1 \left(C_A^{1/2} C_B - \frac{C_D}{K_C} \right) \quad \text{where } K_C = \frac{k_1}{k_2}$$

c)



Low temperatures

$$-r_A = \frac{k P_A P_B}{1 + K_A P_A + K_B P_B}$$

P3-10 cont'd

High temperatures

$$-r_A = \frac{k \left[P_A P_B - \frac{P_C P_D}{K_P} \right]}{1 + K_A P_A + K_B P_B}$$

P3-11



Species	Symbol	Initial Moles	Change in Moles	Final Moles	Concentration
Napthalene	A	F _{AO}	-F _{AO} X	F _{AO} (1-X)	$\frac{F_{AO}(1-X)}{v_{AO}(1+\epsilon X)} \frac{P}{P_o} \frac{T_o}{T}$
Oxygen	B	θ ₃ F _{AO}	-9/2F _{AO} X	F _{AO} (θ ₃ -9/2X)	$\frac{F_{AO}(\theta_3 - 9/2X)}{v_{AO}(1+\epsilon X)} \frac{P}{P_o} \frac{T_o}{T}$
Phthalic Anhydride	C	0	F _{AO} X	F _{AO} X	$\frac{F_{AO} X}{v_{AO}(1+\epsilon X)} \frac{P}{P_o} \frac{T_o}{T}$
Carbon Dioxide	D	0	2F _{AO} X	2F _{AO} X	$\frac{2F_{AO} X}{v_{AO}(1+\epsilon X)} \frac{P}{P_o} \frac{T_o}{T}$
Water	E	0	2F _{AO} X	2F _{AO} X	$\frac{2F_{AO} X}{v_{AO}(1+\epsilon X)} \frac{P}{P_o} \frac{T_o}{T}$
		F _{T0} =F _{AO} (1+θ ₃)		F _T =F _{AO} (1+θ ₃ -5X)	

$$\delta = -1/2 \quad y_{AO} = 0.035 \quad \theta_B = 20.3/3.5 = 5.8 \quad \epsilon = y_{AO} \delta = 0.035 \cdot -1/2 = -0.0175$$

$$v_{AO} = F_{T0} R T / P_o$$

$$C_{T0} = P_o / R T = 10 \text{ atm} / (.08206 \text{ (L} \cdot \text{atm / mol K)} \cdot 500 \text{ K}) = .24 \text{ mol / L}$$

$$C_{AO} = .035 \cdot .24 \text{ mol / L} = .0084 \text{ mol / L}$$

a)

$$(1) \quad P_B = C_B R T = \frac{C_{AO} (\theta_3 - 9/2X)}{(1 + \epsilon X)} R T$$

$$= 0.345 \cdot (5.8 - 9/2X) / (1 - 0.0175X)$$

$$P_D = C_D R T = \frac{2C_{AO} X}{(1 + \epsilon X)} R T$$

$$= 0.689 \cdot X / (1 - 0.0175X)$$

$$(2) \quad C_B = \frac{C_{AO} (\theta_3 - 9/2X)}{(1 + \epsilon X)}$$

$$= \frac{0.0084 (5.8 - 9/2X)}{(1 - 0.0175X)}$$

$$C_A = \frac{C_{AO} (1 - X)}{(1 + \epsilon X)}$$

$$= \frac{0.0084 (1 - X)}{(1 - 0.0175X)}$$

$$(3) \quad v = v_{AO} (1 + \epsilon X) = F_{AO} (1 + \theta_3) (1 + \epsilon X) R T / P_o$$

P3-11 cont'd

b)

$$(1) \quad P_B = C_B R T = \frac{C_{A0}(\theta_B - 9/2X)}{(1 + \epsilon X)} \frac{P R T}{P_0}$$

$$P_D = C_D R T = \frac{2C_{A0} X}{(1 + \epsilon X)} \frac{P R T}{P_0}$$

$$(2) \quad C_B = \frac{C_{A0}(\theta_B - 9/2X)}{(1 + \epsilon X)} \frac{P}{P_0}$$

$$C_A = \frac{C_{A0}(1 - X)}{(1 + \epsilon X)} \frac{P}{P_0}$$

$$(3) \quad v = v_{A0} (1 + \epsilon X) P_0/P$$

$$c) \quad -r_A = k_1 C_A^2 C_B$$

from part a

$$P3 \quad -r_A = k_1 \cdot \frac{C_{A0}^3 (1 - X)^2 \cdot (5.8 - 9/2X)}{(1 + \epsilon X)^3}$$

from part b

$$-r_A = k_1 \cdot \frac{C_{A0}^3 (1 - X)^2 \cdot (5.8 - 9/2X)}{(1 + \epsilon X)^3} \left(\frac{P}{P_0} \right)^3$$

$$d) \quad -r_A = k_1 C_A^2 C_B$$

from part a

$$-r_A = k_1 \cdot \frac{C_{A0}^3 (1 - X)^2 \cdot (9/2 - 9/2X)}{(1 + \epsilon X)^3}$$

from part b

$$-r_A = k_1 \cdot \frac{C_{A0}^3 (1 - X)^2 \cdot (9/2 - 9/2X)}{(1 + \epsilon X)^3} \left(\frac{P}{P_0} \right)^3$$

By using pure oxygen instead of air, the concentration of the reactant are higher and the reaction rate is therefore faster.

e) No answer will be given

P3-12



a) compound	symbol	inlet mole	change	outlet moles
H_2	A	0.5	-0.5X	0.5(1-X)
N_2	B	0.5	$\frac{-0.5X}{3}$	0.5(1-1/3X)
NH_3	C	0	+2/3(0.5X)	1/3 X
Total	T	1.0	-1/3X	1-1/3X

$$b) \quad P_0 = 16.4 \text{ atm} \quad T_0 = 1727^\circ\text{C} = 2000 \text{ K} \quad X = 0.60$$

P3-12 cont'd

assuming isothermal, -isentropic and ideal gases

$$C_{H_2} = C_{AO} \frac{0.5(1-X)}{1 - 1/3 X} \frac{P}{P_0} \frac{T}{T_0} = \frac{n_{AO}}{V_0} \frac{0.5(1-X)}{1 - 1/3 X} = \frac{P_{AO}}{RT} \frac{0.5(1-X)}{1 - 1/3 X}$$

$$C_{H_2} = \frac{Y_{AO} n_0}{RT} \frac{(1-X)}{(1 - 1/3 X)} = \frac{(0.5)(16.4 \text{ atm})}{0.082 \text{ atm} \cdot \text{gmol}^{-1} \cdot \text{K} (2000\text{K})} \frac{(1-0.6)}{(1 - 1/3 (0.6))}$$

$$C_{H_2} = (0.03 \frac{\text{gmol}}{\text{liter}}) (0.5) = 0.015 \text{ gmol/l}$$

$$C_{NH_3} = \frac{(1/3)X}{0.5(1-X)} C_{H_2} = \frac{(1/3)(0.6)}{0.5(1-0.6)} (0.015) \frac{\text{gmol}}{\text{l}} = 0.015 \frac{\text{gmol}}{\text{l}}$$

c) If N_2 were the basis of calculation, the chemical equation would be rewritten as:



The outlet moles of H_2 would then be $0.5(1-3X)$. Sixty percent conversion of N_2 would yield a negative number of moles of H_2 coming out, which is not possible.

H_2 is thus the limiting reagent and the maximum conversion of N_2 possible would be 0.33, giving an outlet number of moles of H_2 equal to zero.

P3-13.



$$Y_{NH_3,0} = 0.15 \quad P = 8.2 \text{ atm} \quad T = 227^\circ\text{C} = 500\text{K}$$

a) Assuming ideal gas law

$$C_{T0} = \frac{n_{T0}}{V_0} = \frac{P_0}{RT_0} = \frac{8.2 \text{ atm}}{0.082 \frac{\text{atm} \cdot \text{gmol}^{-1} \cdot \text{K}}{\text{gmol} \cdot \text{K}} (500\text{K})} = 0.2 \text{ gmol/l}$$

$$b) \quad C_{NH_3,0} = Y_{NH_3,0} C_{T0} = (0.15)(0.2 \text{ gmol/l}) = 0.03 \text{ gmol/l}$$



P3-13 cont'd

Compound	Symbol	Initial	Change	Final
H_2S	A	0.15	$-0.15X$	$0.15(1-X)$
O_2	B	0.18	$-\frac{3}{4}(0.15X)$	$0.18 - \frac{3}{4}(0.15X)$
H_2O	C	0	$+0.15X$	$0.15X$
H_2O	D	0	$+\frac{3}{2}(0.15X)$	$+\frac{3}{2}(0.15X)$
N_2	E	0.67	0	0.67
Total	T	1.00	$+1/4(0.15X)$	$1 + 1/4(0.15X)$

$$\text{Initial } \text{N}_2 = 0.79(1-0.15) = 0.79(0.85) = 0.67$$

$$\text{Initial } \text{O}_2 = 0.85 - 0.67 = 0.18$$

$$1) P_i = y_i P = \frac{\eta_i}{\eta_T} P = 8.2 \text{ atm} \left(\frac{\eta_i}{1 + [0.15/4]X} \right)$$

$$C_i = \frac{\eta_i}{V} = \frac{P_i}{RT} = \frac{\eta_i}{1 + 0.15/4 X} \frac{8.2 \text{ atm}}{0.082 \frac{1 \text{ atm}}{\text{mol} \cdot \text{K}} (500\text{K})} = 0.2 \frac{\text{mol}}{1} \left(\frac{\eta_i}{1 + 0.15/4 X} \right)$$

i.	η_i	P_i (atm)	C_i
A	$0.15(1-X)$	$1.23 \frac{1-X}{1 + [0.15/4]X}$	$0.03 \frac{1-X}{1 + [0.15/4]X}$
B	$0.18 - \frac{3}{4}(0.15X)$	$8.2 \left(\frac{0.18 - 3/4(0.15X)}{1 + [0.15/4]X} \right)$	$(0.036 - \frac{0.15}{4}X) / (1 + \frac{0.15}{4}X)$
C	$0.15X$	$1.23 \frac{X}{1 + \left[\frac{0.15}{4} \right]X}$	$0.03X / (1 + \frac{0.15}{4}X)$
D	$\frac{3}{2}(0.15X)$	$1.83 \frac{X}{1 + [0.15/4]X}$	$0.045 / (1 + \frac{0.15}{4}X)$
E	0.67	$8.49 \frac{1}{1 + [0.15/4]X}$	$0.113 / (1 + \frac{0.15}{4}X)$

P3-13 cont'd

$$\text{check } P_{\text{TOT}} = \frac{1.23 - 1.23X - 8.2(0.15) - (8.2)(9/4)(0.15X) - 1.23X - 1.85X - 1.49}{1 + (0.15/4)X}$$

$$= \frac{8.2 - 0.313X}{1 + (0.15/4)X} = 8.2$$

$$V = V_0 \left(1 + \frac{0.15}{4} X\right)$$

2) Constant volume

$$C_A = 0.2 \eta_1$$

$$P_A = C_A RT = (0.082)(500)(0.2)\eta_1 = 8.2 \eta_1$$

x	η_1	C_A	P_A
A	$0.15(1-X)$	$0.03 (1-X)$	$1.23 (1-X)$
B	$0.15 - \frac{9}{4} (0.15X)$	$0.036 - \frac{0.15}{4} X$	$8.2(0.15 - \frac{9}{4} (0.15X))$
C	$0.15 X$	$0.03 X$	$1.23 X$
D	$\frac{9}{2} (0.15X)$	$0.045 X$	$1.85 X$
I	0.67	0.133	5.49
		$0.199 + 0.008X$	$8.2 - 0.313 X$
		$= 8.2 \left(1 + \frac{0.15}{4} X\right)$	

$$P_{\text{TOT}} = 8.2 - 0.313 X \text{ atm}$$

3) Same as (1)



Mole balance for a PFR

$$\frac{dF_A}{dV} = -r_A$$

$$\frac{dF_B}{dV} = -r_B$$

$$\frac{dF_C}{dV} = -r_C$$

$$\frac{dF_D}{dV} = -r_D$$

Rate Law (assume elementary):

$$-r_A = kC_A^4 C_B^5$$

P3-13 cont'd

Combine with equation 3-40 and 3-48

$$\frac{dF_A}{dV} = k \left(\frac{P_{T0}}{RT_0} \right)^2 \left(\frac{F_A}{F_A + F_B + F_C} \right)^4 \left(\frac{F_B}{F_A + F_B + F_C} \right)^2$$

$$\frac{dF_B}{dV} = \frac{5}{4} k \left(\frac{P_{T0}}{RT_0} \right)^2 \left(\frac{F_A}{F_A + F_B + F_C} \right)^4 \left(\frac{F_B}{F_A + F_B + F_C} \right)^2$$

$$\frac{dF_C}{dV} = -k \left(\frac{P_{T0}}{RT_0} \right)^2 \left(\frac{F_A}{F_A + F_B + F_C} \right)^4 \left(\frac{F_B}{F_A + F_B + F_C} \right)^2$$

$$\frac{dF_D}{dV} = -k \left(\frac{P_{T0}}{RT_0} \right)^2 \left(\frac{F_A}{F_A + F_B + F_C} \right)^4 \left(\frac{F_B}{F_A + F_B + F_C} \right)^2$$

P3-14 Solution

Thermodynamics predicts the reacting species in a reversible reaction are related by the equation given below.

$$K_c = \frac{C_{B,e}}{C_{A,e}}$$

Stoichiometry:

Constant Volume Batch:

$$C_A = \frac{N_{A,0}(1-X)}{V_0} = C_{A,0}(1-X) \quad \text{and} \quad C_B = \frac{2N_{A,0}X}{V_0} = 2C_{A,0}X$$

Plug Flow Reactor (PFR):

$$C_A = \frac{F_{A,0}(1-X)}{v_0(1+\epsilon X)} = C_{A,0} \frac{(1-X)}{(1+\epsilon X)} \quad \text{and} \quad C_B = \frac{2F_{A,0}X}{v_0(1+\epsilon X)} = \frac{2C_{A,0}X}{(1+\epsilon X)}$$

$$\epsilon = y_{A,0}\delta = (y_{A,0})(2-1) = y_{A,0}$$

P3-14 cont'd

Combine and Rearrange:
Constant Volume Batch:

$$X_s = \sqrt{\frac{K_c(1 - X_s)}{4C_{A_s}}}$$

PFR:-

$$X_s = \sqrt{\frac{K_c(1 - X_s)(1 + \epsilon X_s)}{4C_{A_s}}}$$

The equations above were solved using POLYMATH. The equations in POLYMATH notation are shown below.

$$f(xcf) = xcf - ((kc * (1 - xcf) * (1 + eps * xcf)) / (4 * cao))^{.5} - 0.5$$

$$f(xcb) = xcb - (kc * (1 - xcb) / (4 * cao))^{.5} - 0.5$$

$$kc = 0.1$$

$$p0 = 2$$

$$t0 = 340$$

$$cao = (ya0 * p0) / (t0 * 0.082)$$

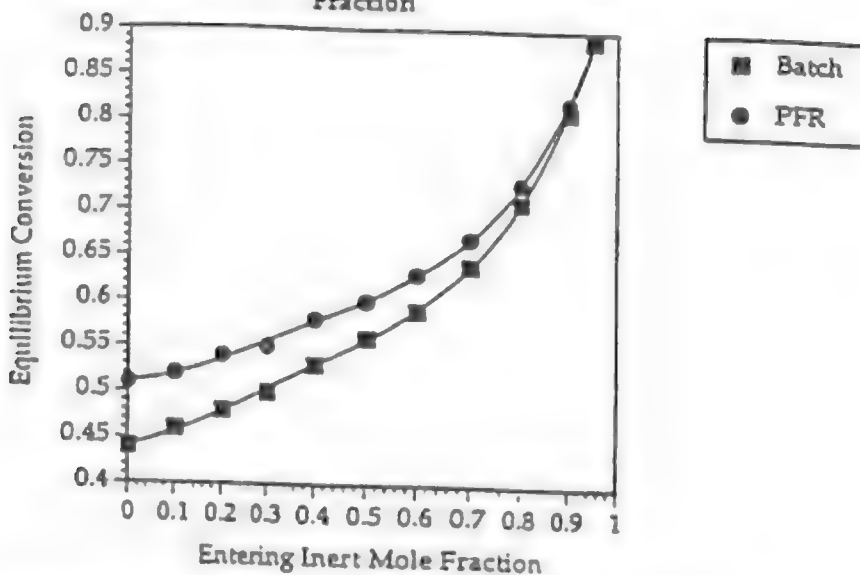
$$eps = ya0$$

$$y10 = 1 - ya0$$

$$ya0 = (\text{number between 0 and 1.0})$$

P3-14 cont'd

Equilibrium Conversion as a
Function of Entering Inert Mole
Fraction



Equilibrium conversion is higher in the PFR because number of moles of gas increases during a reaction, increasing the volume. Since batch is constant volume, change in moles of gas does not influence the system.

If number of moles of gas stays constant PFR and constant volume batch would achieve same equilibrium conversion. If number of moles of gas decreased, constant volume batch would achieve higher equilibrium conversion.

P3-15



$$Y_1 = 0.50, P_0 = 10 \text{ atm}, T_0 = 400^\circ\text{C} = (400 + 273)\text{K} = 673 \text{ K}$$

The kinetic expression for this reaction is

$$r_{\text{HBr}} = \frac{k_1 C_{\text{H}_2} C_{\text{Br}_2}^{\frac{1}{2}}}{k_2 + \frac{C_{\text{HBr}}}{C_{\text{Br}_2}}} \quad \text{from equation 3-18 of the text}$$

$$\delta = 2 - 1 - 1 = 0$$

$$\therefore \epsilon = y_{\text{H}_2} \delta = 0 \text{ and } v = v_0 [P_0/P]$$

$$C_{\text{H}_2,0} = \frac{y_{\text{H}_2} P_0}{RT_0} \quad (\text{all quantities known})$$

P3-15 cont'd

$$\theta_{Br_2} = \frac{N_{Br_2,0}}{N_{H_2,0}} = \frac{y_{Br_2,0}}{y_{H_2,0}} = 1 \quad \theta_{HBr} = 0$$

$$C_{H_2} = \frac{N_{H_2,0}(1-X)}{v} = \frac{N_{H_2,0}}{v_0 f(P/P_0)} (1-X) = \frac{C_{H_2,0}}{f(P/P_0)} (1-X)$$

$$C_{H_2} = \frac{y_{H_2,0} P_0}{RT_0} (1-X)$$

$$C_{Br_2} = \frac{N_{H_2,0}(\theta_B - X)}{v} = \frac{y_{H_2,0} P_0}{RT_0} (1-X)$$

$$C_{HBr} = \frac{N_{H_2,0}(\theta_B + 2X)}{v} = \frac{y_{H_2,0} P_0}{RT_0} (2X)$$

Substituting expressions for C_{H_2} , C_{Br_2} , C_{HBr} into eqn. 3-18

$$r_{HBr} = \frac{k_1 \left(\frac{y_{H_2,0} P_0}{RT_0} \right)^{\frac{1}{2}} (1-X)^{\frac{1}{2}}}{k_2 + \frac{2X}{1-X}} = \frac{k_1 \left(\frac{.25 \cdot 10 \text{ atm}}{0.0821 \text{ atm} \cdot 673 \text{ K}} \right)^{\frac{1}{2}} (1-X)^{\frac{1}{2}}}{k_2 + \frac{2X}{1-X}}$$

$$r_{HBr} = \frac{0.0097 k_1 (1-X)^{\frac{1}{2}} (\text{mole/l})^{\frac{1}{2}}}{k_2 + 2X/(1-X)}$$

(b) Given: $C_6H_5CH(CH_3) \xrightarrow{\quad} C_6H_6 + C_3H_6$, denoted symbolically as:

$C \xrightarrow{\quad} B + P$ with $y_{C,0} = .75$ $y_{I,0} = .25$

$$-r'_C = \frac{2[P_C - P_B P_P / K]}{1 + K_C P_C + P_D K_B}$$

Eqn. 3.19 of text.

P3-15 cont'd

(a) Constant Volume (see next page)

$$C_C = C_{CO} (1-X) ; C_B = C_P = C_{CO} X$$

$$P_C = C_C RT = C_{CO} RT (1-X)$$

$$P_B = C_B RT = C_{CO} RT X = P_P$$

$$-r'_C = \frac{k(C_{CO} RT) \left[(1-X) - \frac{C_{CO}^2 R^2 T X^2}{K} \right]}{1 + K_C C_{CO} RT (1-X) + K_B C_{CO} RT X}$$

$$= \frac{k(C_{CO} RT) \left[(1-X) - \frac{C_{CO} RT X^2}{K} \right]}{1 + C_{CO} RT (K_C (1-X) + K_B X)}$$

Consider the general case in which both P and T are varying

$$\delta = 1 + 1 - 1 = 1 \quad \epsilon = \gamma_{C,O} \quad b = .75 \quad \theta_P = \theta_D = 0$$

From Eqn. S3-7

From Eqn. S3-8

$$C_C = \frac{C_{CO} [1 - X]}{(P_O/P)(T/T_O)[1 + .75X]} ; \quad C_B = C_P = \frac{C_{CO} X}{(P_O/P)(T/T_O)[1 + .75X]}$$

From Eqn. 3.30

$$P_C = C_C RT = \frac{C_{CO} RT (1-X)}{(P_O/P)(T/T_O)[1 + .75X]} = \left[\frac{C_{CO} RT_O P}{P_O} \right] \left[\frac{1-X}{1 + .75X} \right]$$

Similarly for B and P

$$P_B = C_B RT = \frac{C_{CO} RT X}{(P_O/P)(T/T_O)[1 + .75X]} = \left[\frac{C_{CO} RT_O P}{P_O} \right] \left[\frac{X}{1 + .75X} \right]$$

$$P_P = C_P RT = \frac{C_{CO} RT X}{(P_O/P)(T/T_O)[1 + .75X]} = \left[\frac{C_{CO} RT_O P}{P_O} \right] \left[\frac{X}{1 + .75X} \right]$$

P3-15 cont'd

Substitution of above expressions for P_C , P_B , and P_P into rate expression

$$-r'_C = \frac{k_1 \left[\frac{C_{O_2} RT_0 P}{P_0 (1 + .75X)} \right] \left[(1-X) - \frac{1}{K} \left[\frac{C_{CO} RT_0 P}{P_0} \right] \left[\frac{X^2}{1 + .75X} \right] \right]}{1 + k_c \left[\frac{C_{CO} RT_0 P}{P_0} \right] \left[\frac{1-X}{1 + .75X} \right] + K_B \left[\frac{C_{CO} RT_0 P}{P_0} \right] \left[\frac{X}{1 + .75X} \right]}$$

The above expression can be simplified further by noting that

$$P_{CO} = y_{C,O} P_0 = C_{O_2} RT_0 \quad \text{i.e.} \quad y_{C,O} = \frac{C_{O_2} RT_0}{P_0}$$

$$-r'_C = \frac{\left(\frac{k_1 y_{C,O} P}{1 + 0.75X} \right) \left[(1-X) - \frac{1}{K} (y_{C,O} P) \left(\frac{X^2}{1 + 0.75X} \right) \right]}{1 + K_C y_{C,O} P \left(\frac{1-X}{1 + 0.75X} \right) + K_B y_{C,O} P \left(\frac{X}{1 + 0.75X} \right)}$$

P3-16.



$$r = y_{A0} \delta = 0.5(1-1-2) = 0.5(-2) = -1$$

$$-r_A = k C_A C_B$$

$$k = A_0 e^{-E/RT} = 4 \text{ dm}^3/\text{gmol min}$$

$$A = 4 \frac{\text{dm}^3}{\text{gmol min}} \exp \left(\frac{15,000 \text{ cal/gmol}}{1.987 \text{ cal/gmol}^\circ\text{K} (727+273)\text{K}} \right)$$

$$A = 4 \frac{\text{dm}^3}{\text{gmol min}} (1898.97) = 7.60 \times 10^3 \frac{\text{dm}^3}{\text{gmol min}}$$

If we neglect pressure drop

$$v = v_0 \frac{P_0}{P} (1+eX) \frac{T}{T_0} = v_0 (1+eX) = v_c (1-X)$$

P3-16 cont'd

Stoichiometric Table

A	F_{AO}	$-F_{AO}X$	$F_{AO}(1-X)$
B	$F_B = F_{AO}$	$-2F_{AO}X$ $+F_{AO}X$	$F_{AO}(1-2X)$ $F_{AO}X$
C	$2F_{AO}$	$-2F_{AO}X$	$2F_{AO}(1-X)$

a) at $X=0.25$, $v = v_0(1-X) = 2.5 \frac{dm^3}{min} (0.75) = 1.88 dm^3/min$

b) $-r_A = kC_A C_B = kC_{AO} C_{BO}$ at entrance to the reactor

$$-r_A = kC_{AO} C_{BO} = kC_{AO}^2$$

$$C_{AO} = \frac{Y_{AO} P_0}{RT_0} = \frac{0.5(10^5 \text{ atm})}{.08206 \text{ atm l/gmol}^\circ\text{K} (1000)\text{K}} = 6.09 \times 10^{-2} \text{ gmol/l}$$

$$-r_A = 4 \frac{dm^3}{gmol \cdot min} (6.09 \times 10^{-2})^2 \frac{gmol^2}{dm^6} = 1.49 \times 10^{-2} \frac{gmol}{dm^3 \cdot min}$$

c) $-r_A = kC_A C_B = k \frac{F_A F_B}{v^2} = \frac{kF_{AO}(1-X) F_{AO}(1-2X)}{v_0^2 (1-X)^2}$

$$-r_A = kC_{AO}^2 \frac{(1-2X)}{(1-X)}$$

$$-r_A = 4 \frac{dm^3}{gmol \cdot min} (6.09 \times 10^{-2})^2 \frac{gmol^2}{dm^6} \frac{(1-0.8)}{(1-0.4)}$$

$$-r_A = 4.95 \times 10^{-3} \frac{gmol}{dm^3 \cdot min}$$

d) $C_{AO} = 6.09 \times 10^{-2} \text{ gmol/l}$

e) $C_A = \frac{F_A}{v} = \frac{F_{AO}(1-X)}{v_0(1-X)} = C_{AO} = 6.09 \times 10^{-2} \text{ gmol/l}$

f) $k = A e^{-E/RT} = 7.60 \times 10^3 \frac{dm^3}{gmol \cdot min} \exp \left[\frac{-15,000 \text{ cal/gmol}}{1.987 \text{ cal/gmol}^\circ\text{K} \cdot 1500 \text{ K}} \right]$

$$k = 49.6 \frac{dm^3}{gmol \cdot min}$$

P3-16 cont'd

From Equation (E3.7-4), $C_A = \frac{C_{A0}(1-X)}{[1-X]} = C_{A0}$. The concentration of A in the gas phase does indeed remain constant. For each mole of A reacted, one mole of gas condenses (as product D), and hence C_A remains constant. Then considering the reaction as a mixture of both gas and liquid, however, the amount of A in this mixture continually decreases.

P3-17. Solution

(a) liquid phase reaction \rightarrow assume constant volume

Rate Law (reversible reaction):

$$-r_A = k \left[C_A C_B - \frac{C_C}{K_C} \right]$$

Stoichiometry:

$$C_A = C_{A0}(1-X), C_B = C_{A0}(1-X), C_C = C_{A0}X$$

To find the equilibrium conversion, set $-r_A = 0$, combine stoichiometry and rate the rate law, and solve for X_e .

$$C_A C_B K_C = C_C$$

$$C_{A0}^2 (1-X_e)^2 K_C = C_{A0} X_e$$

$$X_e^2 - \left(2 + \frac{1}{C_{A0} K_C} \right) X_e + 1 = 0$$

$$X_e = 0.80$$

To find the equilibrium concentration, substitute the equilibrium conversion into the stoichiometric relations.

$$C_A = C_{A0}(1-X_e) = 2 \text{ mol/dm}^3 (1-0.80) = .4 \text{ mol/dm}^3$$

$$C_B = C_{A0}(1-X_e) = 2 \text{ mol/dm}^3 (1-0.80) = .4 \text{ mol/dm}^3$$

$$C_C = C_{A0} X_e = 2 \text{ mol/dm}^3 (0.80) = 1.60 \text{ mol/dm}^3$$

b)

Stoichiometry:

$$\epsilon = y_{A0} \delta = (1)(3-1) = 2 \text{ and } \theta_C = 0$$

P3-17 cont'd

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0(1+2X)} = C_{A0} \frac{(1-X)}{(1+2X)}$$

$$C_C = \frac{N_C}{V} = \frac{3N_{A0}X}{V_0(1+2X)} = C_{A0} \frac{3X}{(1+2X)}$$

Combine (and solve for X_0):

$$K_C C_{A0} \frac{(1-X_0)}{(1+2X_0)} = \left[C_{A0} \frac{3X_0}{(1+2X_0)} \right]^2$$

$$K_C (1-X_0)(1+2X_0)^2 = 27 C_{A0}^2 X_0^2$$

$$-\left(4 + \frac{27 C_{A0}^2}{K_C}\right) X_0^2 + 3X_0 + 1 = 0$$

$$X_0 = 0.58$$

Find equilibrium concentrations:

$$C_{A0} = \frac{P_0}{RT_0} = \frac{(10 \text{ atm})}{(400 \text{ K}) \left(0.082 \frac{\text{dm}^3 \text{ atm}}{\text{mol K}} \right)} = 0.305 \frac{\text{mol}}{\text{dm}^3}$$

$$C_A = 0.305 \frac{(1-0.58)}{(1+2(0.58))} = 0.059 \frac{\text{mol}}{\text{dm}^3}$$

$$C_C = \frac{3(0.58)(0.305)}{(1+2(0.58))} = 0.246 \frac{\text{mol}}{\text{dm}^3}$$

c) same reaction, rate law, and initial concentration as part (b) gas phase, batch reaction

Stoichiometry:

$$C_A = N_A / V = N_{A0} (1-X) / V_0 = C_{A0} (1-X)$$

$$C_C = N_C / V = 3N_{A0} X / V_0 = 3C_{A0} X$$

Combine and Solve for X_e :

$$K_C C_{A0} (1-X_e) = (3C_{A0} X_e)^2$$

$$X_e = 0.39$$

P3-17 cont'd

Find the equilibrium concentrations:

$$C_{Ae} = (0.305)(1 - 0.39) = 0.19$$

$$C_{Ce} = (0.305)(0.39) = 0.36$$

d) gas phase reaction in a constant pressure, batch reactor

Rate law (reversible reaction):

$$-r_A = k(C_A - C_C^2/K_C)$$

Stoichiometry:

$$\epsilon = y_{A0} \delta = (1)(3-1) = 2 \text{ and } \theta_C = 0$$

$$C_A = N_A / V = N_{A0} (1 - X) / [V_0 (1 + \epsilon X)] = C_{A0} (1 - X) / (1 + 2X)$$

$$C_C = N_C / V = 3N_{A0}X / [V_0 (1 + \epsilon X)] = C_{A0} 3X / (1 + 2X)$$

Combine and solve for X_e:

$$K_C C_{A0} (1 - X_e) / (1 + 2X_e) = [C_{A0} 3X_e / (1 + 2X_e)]^2$$

$$X_e = .58$$

Find equilibrium concentrations:

$$C_A = 0.305 (1 - 0.58) / (1 + 2(0.58)) = 0.059 \text{ mol / dm}^3$$

$$C_C = 3 (0.305) (0.58) / (1 + 2(0.58)) = 0.246 \text{ mol / dm}^3$$

(Solutions by J.T. Santini, Jr.)

P3-18 Given: Gas phase reaction $A + B \rightarrow C$ in a Batch reactor fitted with a piston such that

$$V = 0.1 P_0; \quad k = 1.0 (\text{ft}^3)^2 / \text{lbmol}^2 \text{ sec}$$

$$-r_A = k C_A^2 C_B \quad N_{A0} = N_{B0} \text{ at } t=0$$

$$V_0 = 0.15 \text{ ft}^3 \quad T = 140^\circ\text{C} = 600^\circ\text{R} = \text{Constant}$$

$$(a) \quad y_{A0} = N_{A0} / (N_{A0} + N_{B0}) = 0.5$$

$$\delta = 3 - 1 - 1 = 6$$

$$\epsilon = y_{A0} \delta = 3$$

$$\text{Now} \quad V = V_0 P_0 / P (T / T_0) (1 + \epsilon X)$$

$$T / T_0 = 1$$

$$P = 10V$$

$$\text{therefore} \quad V = 10 V_0^2 / 10V (1 + \epsilon X) \text{ or } V^2 = V_0^2 [1 + \epsilon X]$$

$$P_0 = 10 V_0$$

P3-18 cont'd

$$N_A = N_{A0} (1 - X)$$

$$N_B = N_{A0} (B_0 - X)$$

$$B_0 = N_{B0} / N_{A0} = 1.0$$

therefore

$$-r_A = k C_A^2 C_B = k N_A^2 N_B / V^3 = k N_{A0}^3 (1 - X)^3 / (V_0^3 (1 + \epsilon X)^{3/2}); \quad N_{A0} = (y_{A0} P_0 / RT) V_0$$

therefore

$$-r_A = k \left(\frac{y_{A0} P_0}{RT} \right)^3 \frac{(1 - X)^3}{(1 + \epsilon X)^{3/2}}$$

$$-r_A = 1.0 \text{ (ft}^3\text{)}^2 / ((11 \text{ lbmole})^2 \text{ sec}) \quad [0.75 / (.730 \text{ atm ft}^3/\text{lbmol} \cdot R \cdot 600^\circ R)]^3 \quad \frac{(1 - X)^3}{(1 + 3X)^{3/2}}$$

$$-r_A = 5.03 \cdot 10^{-9} \frac{(1 - X)^3 \text{ lbmol} / \text{ft}^3 \text{ sec}}{(1 + 3X)^{3/2}}$$

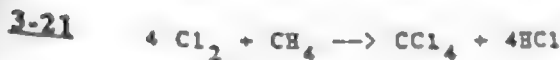
(b) $V = V_0 (1 + \epsilon X)^{1/2}$

$$.2 = 0.15 (1 + 3X)^{1/2} \quad X = .259$$

$$-r_A = 8.63 \cdot 10^{-10} \text{ lbmol} / \text{ft}^3 \text{ sec}$$

P3-12 There will be no solution given.

P3-20 There will be no solution given.



$$T = 75^\circ \text{C} = 348 \text{ K}$$

$$P = 950 \text{ kPa} = 9.39 \text{ atm}$$

$$\text{Cl}_4 \text{ vapor pressure} = 95 \text{ kPa} = 0.94 \text{ atm} = P_v$$

P3-21 cont'd

$$C_i = \frac{F_i}{v} = \frac{F_i}{v_0(1+sX)} = \frac{F_i}{v_0}$$

So we can use the stoichiometric table, substituting C's for F's

i	F_i	C_i
A	$F_{A0}(1-X)$	$C_{A0}(1-X)$
B	$4F_{A0}(1-X)$	$4C_{A0}(1-X)$
C	$4F_{A0}X$	$4C_{A0}X$
D	$F_{A0}X$	$C_{A0}X$
	$5 F_{A0}$	$5 C_{A0}$

where $C_{A0} = 0.0658 \text{ gmol/l}$ and $F_{A0} = 0.02631 \text{ gmol/s}$

After condensation

$$v = v_0 \frac{F_t}{F_{t0}} = v_0 \frac{F_{A0}(5-X)}{5 F_{A0}(0.90)} = v_0 \frac{5-X}{4.5}$$

$$C'_i = \frac{F_i}{v} = \frac{F_i(4.5)}{v_0(5-X)}$$

Note: at $X = 0.5$ (beginning of condensation) $C_i = C'_i$

i	F_i	C_i
A	$5F_{A0} - F_{A0}X$	$C_{A0}(1-X)(4.5)/(5-X)$
B	$F_{A0}(5-X)$	$4C_{A0}(1-X)(4.5)/(5-X)$
C	$4F_{A0}X$	$4C_{A0}X(4.5)/(5-X)$
D	$0.1F_{A0}(5-X)/0.9$	$C_{A0}(5-X)(4.5)/(5-X)/9 = 0.5C_{A0}$
Total	$F_{A0}(5-X) + F_{A0}(5-X)/9$	$C_{A0}(5-X)^2/40.5$

where $F_{A0} = 0.02631 \text{ gmol/s}$ and $C_{A0} = 0.0658 \text{ gmol/l}$

P3-21 cont'd

$$y_{DE} = \frac{P_V}{P} = \frac{95}{950} = 0.10$$



Assume stoichiometric feed F_i

Species	Symbol	In	Change	Before Condensation $P_D < P_V$ remaining	After Condensation $P_D = P_V$ remaining
CH_4	A	F_{AO}	$-F_{AO}X$	$F_A = F_{AO}(1-X)$	$F_{AO}(1-X)$
Cl_2	B	$4F_{AO}$	$-4F_{AO}X$	$F_B = 4F_{AO}(1-X)$	$4F_{AO}(1-X)$
HCl	C	0	$+4F_{AO}X$	$F_C = 4F_{AO}X$	$4F_{AO}X$
CCl_4	D(g)	0	$+F_{AO}X$	$F_D = F_{AO}X$	$0.10F_T$
	D(l)	0	—	—	—
$F_{TO} = 5F_{AO}$				$F_T = 5F_{AO}$	$F_T' = 5F_{AO} - F_{AO}X + 0.10F_T'$
					$F_T' = \frac{F_{AO}(5-X)}{0.90}$

When condensation first begins $F_T = F_T'$

$$5F_{AO} = F_{AO} \frac{(5-X)}{0.90} \rightarrow X_c = 0.50$$

Before Condensation

$$z = y_{AO} \delta \quad \delta = 0 \rightarrow z = 0$$

$\Delta T = \Delta P = 0 \rightarrow$ Total concentration is constant

$$C_T = C_{T0} = \frac{P_0}{RT_0} = \frac{9.39 \text{ atm}}{0.08205 \frac{\text{atm lit}}{\text{gmol K}} \times 348 \text{ K}} = 0.329 \frac{\text{gmol}}{\text{lit}}$$

$$C_{AO} = \frac{1}{5} C_{T0} = \frac{0.329}{5} \text{ gmol/l} = 0.0658 \text{ gmol/l}$$

$$F_{AO} = C_{AO} v_0 = (0.0658) \text{ gmol/l} (0.4) \text{ l/s} = 0.02631 \text{ gmol/s}$$

P3-22



$$T = 200^\circ\text{C} = 473 \text{ K}$$

$$P = 2500 \text{ kPa} = 24.7 \text{ atm}$$

$$P_{V, \text{C}_2\text{H}_4\text{Br}_2} = 506.5 \text{ kPa}$$

$$y_{DE} = \frac{P_v}{P} = \frac{506.5}{2500} = 0.203$$

Stoich table



assume stoichiometric feed

Species	Symbol	In	Change	F_i before condensation P_D < P_v remaining	F'_i After condensation $P_D =$ P_v remaining
C_2H_6	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$	$F_{A0}(1-X)$
Br_2	B	$2F_{A0}$	$-2F_{A0}X$	$F_B = 2F_{A0}(1-X)$	$2F_{A0}(1-X)$
HBr	C	0	$2F_{A0}X$	$F_C = 2F_{A0}X$	$2F_{A0}X$
$\text{C}_2\text{H}_4\text{Br}_2$	D(g)	0	$F_{A0}X$	$F_D = F_{A0}X$	$0.203F'_T$
	D(l)	0	-	-	-
		$F_{T0} = 3F_{A0}$		$F_T = 3F_{A0}$	$F'_T = 3F_{A0} - F_{A0}X + 0.203F'_T$

when condensation first begins $F_T = F'_T$

$$F'_T = \frac{F_{A0}(3-X)}{0.797}$$

$$3F_{A0} = \frac{F_{A0}(3-X)}{0.797} \rightarrow X_C = 0.609$$

Before condensation

$$z = y_{A0}^5 \quad \delta = 0 \rightarrow z = 0$$

$\Delta T = \Delta P = 0$ So total concentration is constant

$$C_T = C_{T0} = \frac{P_0}{RT_0} = \frac{24.7 \text{ atm}}{0.08205 \frac{\text{atm lit}}{\text{gmol K}} \times 473 \text{ K}} = 0.673 \text{ gmol/l}$$

$$C_{A0} = \frac{1}{3} C_{T0} = \frac{0.673}{3} \text{ gmol/l} = 0.222 \text{ gmol/l}$$

3-35

i	F_i	C_i
A	$F_{AO}(1-X)$	$C_{AO}(1-X)(2.39)/(3-X)$
B	$2F_{AO}(1-X)$	$2C_{AO}(1-X)(2.39)/(3-X)$
C	$2F_{AO}X$	$2C_{AO}(X)(2.39)/(3-X)$
D	$F_{AO}(3-X)/3.93$	$C_{AO}(0.609)$
Total	$F_{AO}(3-X)/0.797$	

where $F_{AO} = 0.106 \text{ gmol/s}$ and $C_{AO} = 0.212 \text{ gmol/l}$

X	F_A gmol/s	F_B gmol/s	F_C gmol/s	F_D gmol/s	F_T gmol/s	C_A gmol/l
X	$F_{AO}(1-X)$	$2F_{AO}(1-X)$	$2F_{AO}X$	$F_{AO}X$	$3F_{AO}$	$C_{AO}(1-X)$
0	0.106	0.212	0	0	0.318	0.212
0.2	0.085	0.170	0.042	0.021	0.318	0.170
0.4	0.064	0.127	0.083	0.041	0.318	0.127
0.609	0.041	0.083	0.129	0.063	0.318	0.083
X	$F_{AO}(1-X)$	$2F_{AO}(1-X)$	$2F_{AO}X$	$F_{AO} \frac{(3-X)}{3.93}$	$F_{AO} \frac{(3-X)}{0.797}$	$C_{AO} \frac{(1-X)(2.39)}{(3-X)}$
0.609	0.041	0.083	0.129	0.063	0.318	0.083
0.8	0.021	0.042	0.170	0.059	0.293	0.039
1.0	0	0	0.212	0.054	0.266	0

C_B gmol/l	C_C gmol/l	C_D gmol/l
$2C_{AO}(1-X)$	$2C_{AO}X$	$C_{AO}X$
0.414	0	0
0.339	0.083	0.042
0.254	0.170	0.083
0.166	0.258	0.129
$2C_{AO} \frac{(1-X)(2.39)}{(3-X)}$	$2C_{AO} \frac{(2.39)}{(3-X)}$	$C_{AO} (0.609)$
0.166	0.258	0.129
0.078	0.312	0.109
0	0.354	0.090

P3-22 cont'd

$$F_{AO} = C_{AO} v_o = (0.212) \text{ gmol/l} (0.5) \text{ l/s} = 0.106 \text{ gmol/s}$$

$$C_i = \frac{F_i}{v} = \frac{F_i}{v_o(1+X)} = \frac{F_i}{v_o}$$

So we can first use the stoichiometric table, substituting C's for F's

i	F_i	C_i
A	$F_{AO}(1-X)$	$C_{AO}(1-X)$
B	$2F_{AO}(1-X)$	$2C_{AO}(1-X)$
C	$2F_{AO} X$	$2C_{AO} X$
D	$F_{AO} X$	$C_{AO} X$
Total	$3 F_{AO}$	$3 C_{AO}$

where $F_{AO} = 0.106 \text{ gmol/s}$ and $C_{AO} = 0.212 \text{ gmol/s}$

After condensation

$$v = v_o \frac{F_t}{F_{to}} = v_o \frac{F_{AO} (3-X)}{3F_{AO}} = v_o \frac{(3-X)}{2.39}$$

$$C'_i = \frac{F_i}{v} = \frac{F_i (2.39)}{v_o (3-X)}$$

Note that at $X = 0.609$ (beginning of condensation) $C_i = C'_i$

P3-22 cont'd

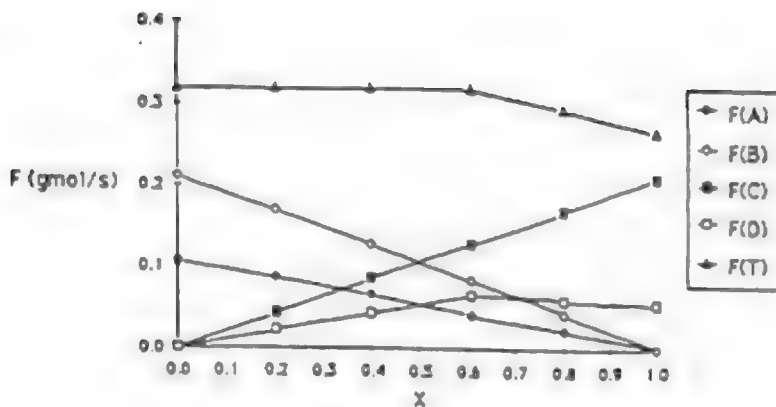


Figure P3-22a

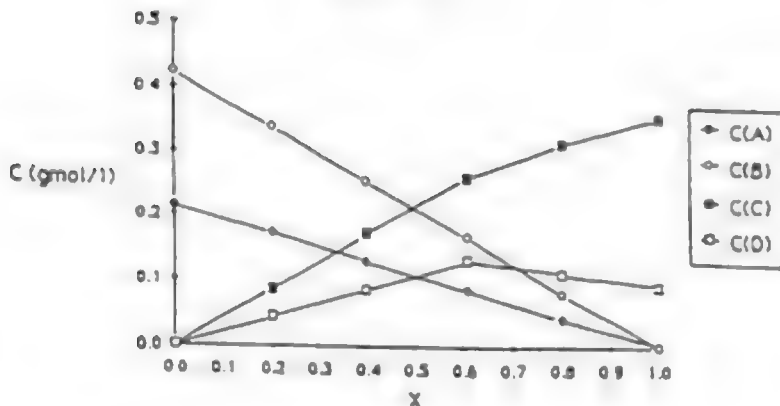


Figure P3-22b

P3-23

Species	Symbol	Entering	Change	Leaving
SiH_4	A	F_{A0}	$-3F_{A0}$	$F_{A0}(1-X)$
NH_3	B	$F_{B0} = 6F_{A0}$	$-4F_{A0}X$	$F_{A0}(6-4X/3)$
Si_2N_4	C	0	$F_{A0}X$	$F_{A0}X/3$
H_2	D	0	$12F_{A0}X$	$4F_{A0}X$

$$\theta_B = \frac{F_{B0}}{F_{A0}} = 1$$

$$y_{A0} = 0.5$$

$$\varepsilon = y_{A0}\delta = 0.5(1+12-3-4) = 3$$

P3-23 cont'd

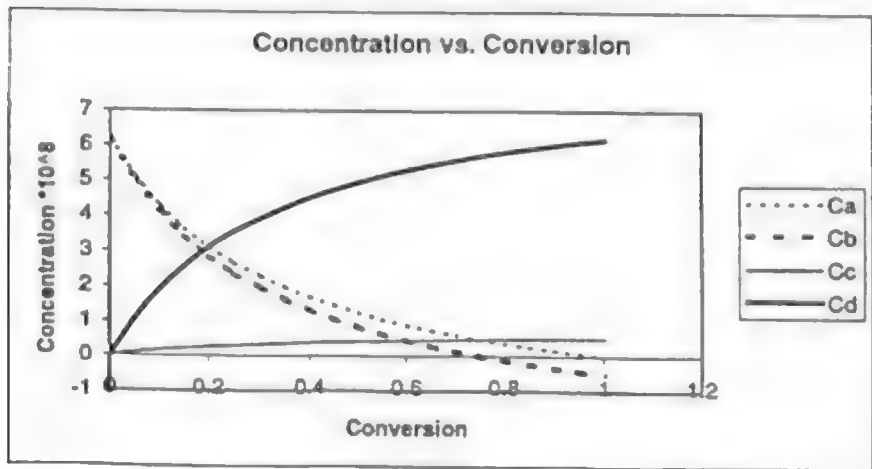
$$C_{A0} = y_{A0} C_{T0} = 0.5 \left(\frac{P_0}{RT_0} \right) = 0.5 \left(\frac{1 \text{ Pa}}{8314 \frac{\text{Pa} \cdot \text{dm}^3}{\text{mol} \cdot \text{K}} \cdot 973 \text{ K}} \right) = 6.18 \cdot 10^{-8}$$

$$C_A = \frac{C_{A0}(1-X)}{1+\epsilon X} = \frac{6.18 \cdot 10^{-8}(1-X)}{1+3X}$$

$$C_B = \frac{1.68 \cdot 10^{-8} \left(1 - \frac{4X}{3} \right)}{1+3X}$$

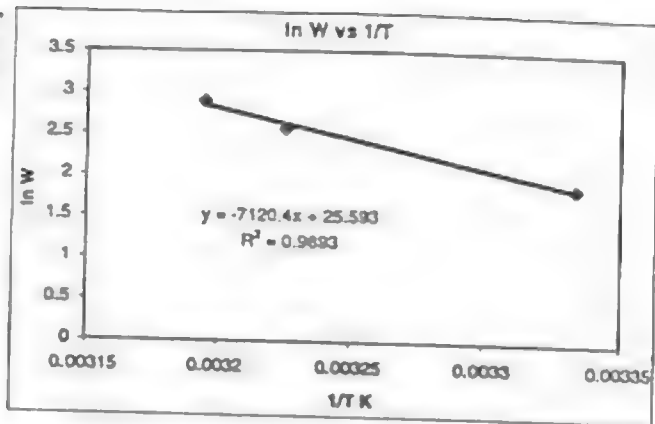
$$C_C = \frac{2.06 \cdot 10^{-8} X}{1+3X}$$

$$C_D = \frac{2.47 \cdot 10^{-8} X}{1+3X}$$



CDP3-A

W	lnW	T	1/T
6.5	1.871802	300	0.003333
13	2.564949	310	0.003226
18	2.890372	313	0.003195



From the graph:

$$E = 7120$$

$$\ln W = -7120.4 \cdot \left(\frac{1}{41.5 + 273} \right) + 25.593 = 2.95$$

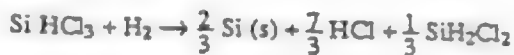
$$W(41.5^\circ\text{C}) = 19.2 \text{ cm/s}$$

CDP3-B

a)



Take Si HCl_3 as basis



CDP3-B cont'd

Species	Symbol	Entering	Change	Leaving
$\text{Si HCl}_3 \text{ (g)}$	A	F_{AO}	$-F_{AO}X$	$F_A = F_{AO}(1-X)$
$\text{H}_2 \text{ (g)}$	B	$F_{BO} = \theta_B F_{AO}$	$-F_{AO}X$	$F_B = F_{AO}(\theta_B - X)$
$\text{H}_2\text{HCl (g)}$	C	0	$+\frac{7}{3}F_{AO}X$	$F_C = \frac{7}{3}F_{AO}X$
$\text{Si H}_2\text{Cl}_2 \text{ (g)}$	D	0	$+\frac{1}{3}F_{AO}X$	$F_D = \frac{1}{3}F_{AO}X$
Si (s)	S	0	$\frac{2}{3}F_{AO}X$	—

Assume isothermal and constant pressure. Neglect the vapor pressure of Si(s)

$\theta_B = 1$ Stoichiometric feed

δ only involves the changes in gas phase

$$\epsilon = y_{AO} \delta = \frac{1}{2} \left(\frac{1}{3} + \frac{7}{3} - 1 - 1 \right)$$

$$\epsilon = \frac{1}{2} \left(\frac{2}{3} \right) = \frac{1}{3}$$

$$C_{AO} = y_{AO} \frac{P_0}{R T_0} = \frac{1}{2} \left(\frac{2.0}{(0.082)(1327)} \right) \quad C_{AO} = 0.0088 \text{ mol/dm}^3$$

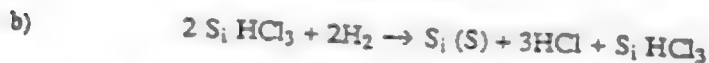
$$C_A = \frac{F_A}{v} = C_{AO} \frac{(1-X)}{(1+\epsilon X)} = \frac{0.0088(1-X)}{1+X/3}$$

$$C_B = \frac{F_B}{v} = C_A \frac{(\theta_B - X)}{(1+\epsilon X)} = \frac{0.0088(1-X)}{1+X/3}$$

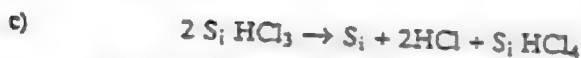
$$C_C = \frac{F_C}{v} = \frac{7}{3} \frac{F_{AO}X}{v_0(1+\epsilon X)} = \frac{7}{3} C_{AO} \frac{X}{(1+\epsilon X)} = 0.021 \frac{X}{(1+X/3)}$$

$$C_D = \frac{F_D}{v} = \frac{1}{3} \frac{F_{AO}X}{v_0(1+\epsilon X)} = 0.0031 \frac{X}{1+X/3}$$

The solution to parts (b) and (c)



and



are similar to Part (a).

CDP3-C Given : $A + B \rightarrow C$ taking place in a square duct.

$$P_O = 1 \text{ atm.} = \text{constant}$$

$$k = 10^6 \text{ ft}^3 / (\text{lb.mole})(\text{sec.})$$

$$T = T_O = 540^\circ\text{F} = 1000^\circ\text{R}$$

$$P_B^* = 0.25 \text{ atm.}$$

$$F_{AO} = 1.5 \text{ lb mole/sec.}$$

(a) If B is at equilibrium in the gas phase throughout the reactor

$C_B = \frac{P_B^*}{RT} = \text{constant}$. Since B maintains its equilibrium vapor pressure throughout the reactor, as soon as 1 molecule of B is consumed by the reaction, it is replaced by a molecule of B in the liquid. Hence, $\delta = 1 - 1 = 0$, $\epsilon = Y_{AO} \delta$.

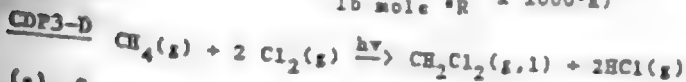
$$-r_A = k C_A C_B = k C_{BO} C_{AO} [1-X]; \text{ Just inside the reactor.}$$

$$C_{AO} = \frac{Y_{AO} P_O}{RT} = \frac{(1-Y_{BO}) P_O}{RT}$$

$$\therefore -r_A = k C_B = k Y_{BO} [1-Y_{BO}] \left(\frac{P_O}{RT} \right)^2 (1-X)$$

(b) At $X = 0.5$

$$-r_A = \frac{10^6 \text{ ft}^3}{(\text{lbmole})(\text{sec})} \left[\frac{(0.25 \text{ atm})(0.75 \text{ atm})}{(0.730 \text{ atm ft}^3 / \text{lb mole} \cdot \text{R} \times 1000^\circ\text{R})^2} \right] [0.5] = .174 \frac{\text{lbmole}}{\text{ft}^3 \text{ sec.}}$$



COMPONENT	Symbol	Initial moles	Change	Out
Cl ₂	A	1.0	-X	1-X
CH ₄	B	0.5	-0.5X	0.5(1-X)
CH ₂ Cl ₂	C	0	+0.5X	0.5X
HCl	D	0	+X	X
Total	T	1.5		1.5

(b) $\delta = 1 + 2 - 1 - 2 = 0$; $Y_{AO} = 1.0$

$\epsilon = Y_{AO} \delta = 0$

CDP3-D

cont'd

(c) System is gas phase until $P_c = 400 \text{ mmHg}$

$$\frac{0.5X'}{1.5} (760) = 400$$

$\therefore X' = 1.5789 \rightarrow \text{CH}_2\text{Cl}_2$ does not condense at 1 atm.

$$k = 0.2 \left(\frac{\text{dm}^3}{\text{gmole}} \right)^2 \frac{1}{\text{s}} \rightarrow \text{3rd order}$$

$$-r_A = k C_A^2 C_B$$

$$C_A = C_{A0} (1 - X_A)$$

$$C_B = \frac{1}{2} C_{A0} (1 - X_A)$$

$$-r_A = \frac{1}{2} k C_{A0}^3 (1 - X_A)^3$$

$$(d) C_{A0} = y_{A0} \frac{P}{RT}$$

$$C_{A0} = \frac{1}{1.5} = \frac{1}{0.08206} \frac{1}{298.2} = 0.02724 \frac{\text{gmol}}{\text{dm}^3}$$

$$C_A = C_{A0} (1 - X_A) = 0.02724 (1 - 0.6) = 0.01090 \frac{\text{gmol}}{\text{dm}^3}$$

$$(e) -r_A = \frac{1}{2} k C_{A0}^3 (1 - X_A)^3$$

$$-r_A = \frac{1}{2} (0.2) (0.02724)^3 (1 - 0.6)^3$$

$$-r_A = 1.297 \times 10^{-7} \frac{\text{gmol}}{\text{dm}^3 \text{ s}}$$

$$(f) k = A \exp \left(-\frac{E}{RT} \right)$$

$$A = 2 \times 10^{12} \frac{\text{dm}^6}{\text{s gmol}^2}$$

$$0.2 = 2 \times 10^{12} \exp \left(\frac{-E}{(8.314)(298.2)} \right) \text{ at } 25^\circ\text{C}$$

$$E = 74212 \frac{\text{J}}{\text{gmol}}$$

(g) At $100^\circ\text{C} = 373.2^\circ\text{K}$

$$\frac{k_{100}}{k_{25}} = \exp \left\{ -\frac{E}{R} \left(\frac{1}{373.2} - \frac{1}{298.2} \right) \right\} = 409.8$$

$$k_{100^\circ\text{C}} = 81.95 \left(\frac{\text{dm}^3}{\text{gmol}} \right)^2 \frac{1}{\text{s}}$$

3-43



a)

Species	Symbol	Initial moles	Change	Final moles	Concentration
Benzoyl chloride	A	N_{A0}	$-N_{A0}X$	$N_{A0}(1-X)$	$N_{A0}(1-X)/V$
Ammonia	B	$N_{A0}\theta_B$	$-2N_{A0}X$	$N_{A0}(\theta_B - 2X)$	$N_{A0}(\theta_B - 2X)/V$
Benzylamide	C	$N_{A0}\theta_C$	$N_{A0}X$	$N_{A0}(\theta_C + X)$	$N_{A0}(\theta_C + X)/V$
Ammonium Chloride	D	$N_{A0}\theta_D$	$N_{A0}X$	$N_{A0}(\theta_D + X)$	$N_{A0}(\theta_D + X)/V$

$$b) C_{A0} = N_{A0}/V = 2 \text{ g mol/l}$$

$$\theta_B = C_{B0}/C_{A0} = 6/2 = 3$$

$$X = \frac{N_{A0} - N_A}{N_{A0}}$$

$$\theta_C = \theta_D = 0$$

$$X = 0.25$$

$$\text{Final conc. of ammonia} = \frac{N_{A0}}{V} (\theta_B - 2X) = 2(3 - 2(0.25)) = 5 \text{ g mol/l}$$

$$\text{Final conc. of benzylamide} = \frac{N_{A0}}{V} (\theta_C + X) = 2(0 + 0.25) = 0.5 \text{ g mol/l}$$

c) Stoichiometric table for a flow system using ammonia as the basis



Species	Symbol	Entering	Change	Exit	Concentration
Ammonia	B	F_{B0}	$-F_{B0}X$	$F_{B0}(1-X)$	$F_{B0}(1-X)/v_0$
Benzoyl chloride	A	$\theta_A F_{B0}$	$-F_{B0}X/2$	$F_{B0}(\theta_A - X/2)$	$F_{B0}(\theta_A - X/2)/v_0$
Benzylamide	C	$\theta_C F_{B0}$	$F_{B0}X/2$	$F_{B0}(\theta_C + X/2)$	$F_{B0}(\theta_C + X/2)/v_0$
Ammonium Chloride	D	$\theta_D F_{B0}$	$F_{B0}X/2$	$F_{B0}(\theta_D + X/2)$	$F_{B0}(\theta_D + X/2)/v_0$

Table for the flow system using ammonia as the basis is different from the original in the following ways.

1) Molar flow rates considered rather than number of moles.

2) $\theta_1 = F_{i0}/F_{B0}$, as opposed to N_{i0}/N_{A0}

3) Concentration found by dividing the exiting molar flow rate by the volumetric flow rate v_0 .

Chapter 4

General: I feel one of the purposes of the homework problem is to encourage the students to re-read the text and lecture notes. The problems in this chapter reinforce the algorithm that will be used throughout reaction engineering.

P4-1. This problem gives the guidelines for the students to develop original problems. If you think other guidelines should be added send me an e-mail (sfogler@umich.edu) and I will see if they can be added to the next printing.

P4-2. I would suggest assigning (a), perhaps (i) or (k) and then only one or two parts (b) through (j). The ones that are assigned could be alternated from year to year.

P4-3. Shows a CRE application in the food industry.

P4-4. Many of our students are taking jobs in the food industry and General M₁ provided this problem to give an example of reaction kinetics in the food industry. This is a fairly straight forward problem.

P4-5. Liquid phase reaction in which parts (a-d) are quite straight forward and provide a reinforcement of the CRE principles. Applied to a PFR and CSTR. Part (e) is open-ended and requires some judgment. (There is not necessarily one exact answer for part (e), it depends on the reactor down time is chosen for emptying and filling and cleaning the reactor.) The problems given alternates are equally straight forward. The only problem more straight forward than this one is CDP4-J_B.

P4-6. Real liquid phase reaction and data. Parts (a-d) are fairly straight forward and provide reinforcement of principles for liquid phase reactions. Part (e) is open-ended and is similar to part (e) for P4-4. P4-4 and P4-5 could be alternated from year to year.

P4-7. A gas phase reaction with a change in the total number of moles and volumetric flow rate v . If either P4-4 or P4-5 is assigned at the same time as this problem, I would suggest assigning only parts (a) and (b) and perhaps part (e). In part (e) they must solve for X and different temperatures to find the optimum. (Also see CDP4-F_A for a gas phase reaction with a change in the total number of moles. Problem CDP4-F_A, which was often assigned from the second edition, is straight forward and reinforces the CRE principles and can be alternated from year to year with P4-7 problem.)

P4-8. This problem is somewhat open-ended and requires some creativity to figure why the pressure conversion is GREATER than the predicted conversion. Ask the students to do some brainstorming. Depending on the time available, I would only assign part (a), especially if part (e) of P4-7 is assigned at the same time.

P4-9. Troubleshooting Problem. Students need to brainstorm ideas of what could be wrong with the reactor. Troubleshooting problems are being given to our students more and more as first or second assignments in industry. Perhaps point out Kepner-Tregoe Strategies (See Ch.5 *Strategies for Creative Problem Solving*, , Prentice Hall, 1995).

P4-10. Parts (a), (b), and (c) are straight forward to calculate PFR and CSTR volumes and a batch reaction time. Part (d) is similar to Part (e) of **P4-4** and **P4-5**. This problem could be alternated with **P4-4** and **P4-5** from year to year.

Problems P4-11, P4-12, P4-13, P4-14, and P4-15. These problems are great motivators for the students because they show the competency level to obtain they must rise to pass the professional engineers exam. A few years ago, and it still may be true. The California exam was one of the toughest, if not the toughest in the nation. There was no curve, you had to have 75% to pass. There were six problems (stoichiometry, fluids, thermo, heat transfer, reaction engineering, and plant design) and you were given 3 hours (1/2 hour per problem).

P4-16. This problem requires a bit of thinking and manipulation of equations.

P4-17. The student cannot use any of the equations presented in the text thus far and must use a model balance to derive a new equation relating conversion and distance. This problem also serves as a motivational problem because it shows how CRE principles are applied to the new field of ECOLOGICAL ENGINEERING. Parts of this problem are solved on the web module "Wetlands".

Problems P4-18, P4-19, P4-20, P4-21, P4-22, P4-23, and P4-24. are all problems involving pressure drop.

P4-18. Straight forward reinforcement of CRE principles. This problem is similar to **P4-22**.

P4-19. Trial and error solution using POLYMATH neither the specific reaction rate constant, k , or the pressure drop parameter, α , are given.

P4-20. Trial and error using POLYMATH. This problem is a much shorter version of the analysis required in **P4-21**.

P4-21. Parts (a) and (b) are straight forward, plug and chug calculations. Parts (c) through (g) requires some analysis. This problem can be quite long depending on how many parts are assigned.

P4-22. Fairly straight forward problem using POLYMATH. Alternate to **P4-20**.

- P4-23. Tough problem. Need to solve for the conversion several times to plot conversion vs. particle diameter in order to find the optimum catalyst size.
- P4-25. Reinforces that the algorithm can be applied to a reactor of a completely different slope, a spherical reactor. Fairly straight forward problem using POLYMATH.
- P4-26. This straight forward problem is the recommended problem to assign to reinforce the principles of semibatch reactors.
- P4-27. This problems is an alternative to P4-26. Also see CDP4-I₈ and CDP4-J₈.
- P4-28. Tough problem involving CSTR with recycle.
- P4-29. Apply the unsteady state mole balances to three CSTRs in series. Use POLYMATH to solve three coupled ODEs.
- P4-30. Membrane reactor. There should be enough time for the students to carry out part (d) parameter variation and ask "What if . ." questions.
- P4-31. Membrane reactor problem that is an alternative to P4-30.
- CDP4-A Good problem concerning batch reactions. solved on the web.
- CDP4-B Alternative to problem P4-17.
- CDP4-C Reversible batch reaction.
- CDP4-D Alternative to CDP4-13.
- CDP4-E California problem that takes 30 minutes to solve.
- CDP4-F Very straight forward problem. Good to reinforce principles
- CDP4-G Optimization problem - not too straight forward.
- CDP4-H Very straight forward batch reactor.
- CDP4-I Semibatch - alternative to P4-26.
- CDP4-J Most straight forward problem in the chapter.
- Problems CDP4-K through CDP4-M all involve recycle.
- CDP4-N Radial flow reactor. New equations must be derived.
- CDP4-O Bacteria growth in a batch reactor.

CDP4-P Fairly straight forward California registration problem where you must carry out a number of calculations involving conversion factors to calculate CSTR and PFR reactor volumes and a batch reaction time.

CDP4-Q I might assign this again if hell freezes over.

Summary

	<u>Assigned</u>	<u>Alternates</u>	<u>Difficulty</u>	<u>Time</u>	<u>Solution Given</u>
P4-1	O	8		--	No
● P4-2				30	Yes
P4-3	I		SF	20	Yes
P4-4	I	A,C,D,O	SF	30	Yes
● P4-5		7(a,b),10(a,b),F,H,I	SF	60	Yes
● P4-6		7,10,16,	FSF	75	Yes
P4-7	AA	5,6,F,G,H,I	FSF	60	Yes
● P4-8		1		25	Yes
P4-9	O			25	Yes
P4-10	AA	5,6,7,F,G,H	FSF	60	Yes
P4-11	AA	12,13,14,15,E	FSF	40	Yes
● P4-12	AA	11,13,14,15,E	FSF	40	Yes
● P4-13	AA	11,12,14,15,E	FSF	40	Yes
P4-14	AA	11,12,13,15,E	FSF	40	Yes
P4-15	AA	11,12,13,14,E	FSF	40	Yes
P4-16	I	5,A,C,D		30	Yes
P4-17	O	B		35	Yes
● P4-18	AA	19,24	SF	45	Yes
P4-19	AA	18,24	SF	45	Yes
P4-20	AA	21,22,23		60	Yes
P4-21	AA	20,22,23		60	Yes
P4-22	AA	20,21,23	FSF	60	Yes
● P4-23	AA	20,21,22	FSF	75	Yes
P4-24	I			45	Yes
● P4-25				2	Yes
P4-26	AA	27,I,J,Q		60	Yes
P4-27	AA	26,I,J,Q		60	Yes
P4-28	S			50	Yes
P4-29	S			60	Yes
P4-30	AA	31		45	Yes
P4-31	AA	30		45	Yes
CDP4-A	AA	4,C,D	SF	45	Yes
CDP4-B		17	SF	45	Yes
CDP4-C	AA	A,D,O,4	SF	45	Yes
CDP4-D	AA	A,C,O,4	SF	45	Yes
CDP4-E	AA	11,12,13,14,15		40	Yes

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● CDP4-F	A	4,J	SF	60	Yes
CDP4-G	AA	F,H,5,6,7,10,	SF	30	Yes
CDP4-H				30	Yes
CDP4-I	AA	26,27,Q		60	Yes
● CDP4-J		26,27,Q		45	Yes
CDP4-K		L,M		50	Yes
CDP4-L		K,M		50	Yes
CDP4-M		K,L		50	Yes
CDP4-N				50	Yes
CDP4-O	AA	A,C,4		50	Yes
CDP4-P				60	Yes
CDP4-Q		26,27,I,J		45	Yes

Assigned

- = Always assigned, AA = Always assign one from the group of alternates, O = Often, I = Infrequently, S = Seldom, G = Graduate level

Alternates

In problems that have a dot in conjunction with AA means that one of the problems, either the problem with a dot or any one of the alternates are always assigned.

Time

Approximate time in minutes it would take a B/B* student to solve the problem.

Difficulty

SF = Straight forward reinforcement of principles (plug and chug)

FSF = Fairly straight forward (requires some manipulation of equations or an intermediate calculation).

IC = Intermediate calculation required

M = More difficult

OE = Some parts open-ended.

*Note the letter problems are found on the CD-ROM. For example A = CDP1-A.

Table 4.1 Solution Manual

	CSTR	PFR	Membrane Reactor	PBR ΔP	Batch Reactor	Semibatch Reactor
Liquid Phase	5,6,8,28	5,6,17			3,6,7,10	26,27
Gas Phase	9,10	7,10		18,19,20, 21,22,23, 24		
Straight Forward	7(a),10(c), F,J	5(a,b), 10(b),18	30,31	18,20	4,5(b,c), 10(a),C,D, H	26,27
Fairly Straight Forward	3	11		20	10(e),A	
More Difficult	7(d),14,16, B,P	2(h),7(d), 13,15,19, P,N		23,24	3,5(e),6(e), 7(c,d),E,O	
Intermediate Calculations		12,13,14		19		
Parameter Variation	7(e),8(b), 29(e)	17(d)	2(f),30(e)	2		26(e)
Competing Effects	6(e),7(e)			23		
Open-ended	2(j,k),8,9, 17(f)		31(e)		6(e)	
Critical Thinking	4(i),5(f), 19(c)	4(f),5(f)		20(c)	26(f), 27(d)	

P4-1 No solution will be given.

P4-2

(a) Cooking food (effect of temperature), removing a stain with bleach (effect of bleach concentration), dissolution of sugar in coffee or tea.

(b) Accept catalyst:

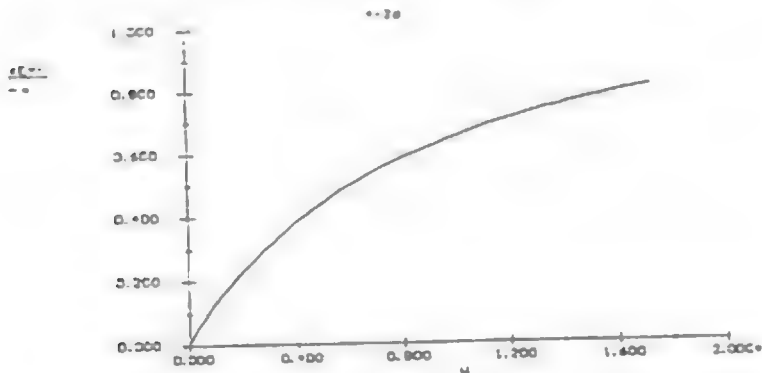
- 1) X is small and pressure drop is unaffected
- 2) cost savings

Reject catalyst:

- 1) Pressure drop now too high therefore lower conversion
- 2) Catalyst not as active as it should be

(c) Bad idea for 100 tubes in series. Pressure drop will be too great because of greater mass flow rate through a single tube and because of the tube length.

(d) Using POLYMATH and the set of equations given in example 4-8, graph conversion as a function of catalyst weight:



$$\alpha = \frac{2\beta_0}{A_c \rho_c (1-\phi) P_0} \quad (4-29)$$

$$\beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3} [\text{small} + 1.75G] \quad (\text{E4-8.7})$$

$$\frac{\beta_0}{P_0} = \frac{1}{DP_0}$$

$$\frac{1}{\frac{1}{5} \cdot \frac{5}{1}} = 1$$

Therefore, there is no effect. In future experiments, run it so that they do not increase and decrease at the same rate.

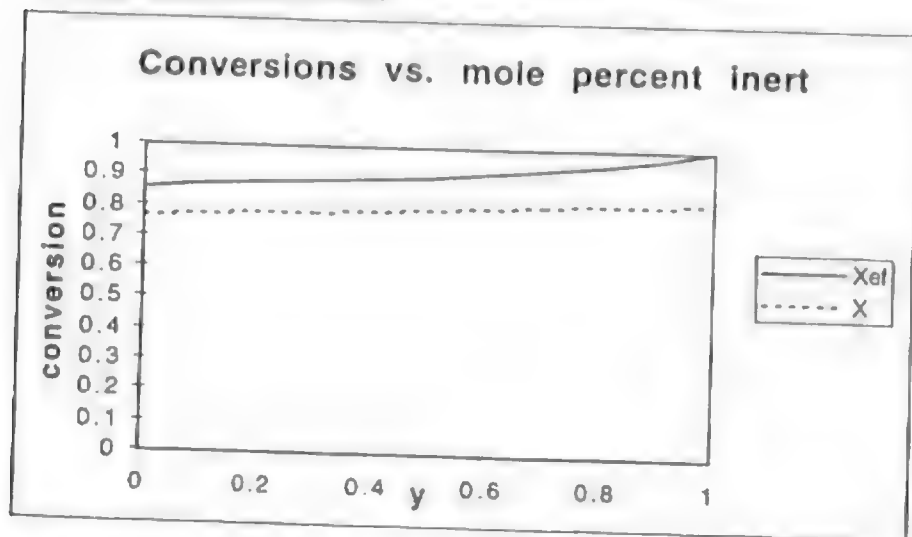
e) To determine the equilibrium conversion use the following equation

$$X_{ef} = \sqrt{\frac{K_c \cdot (1 - X_{ef}) \cdot (1 + \varepsilon X)}{4C_{A0}}}$$

have C_{A0} be a function of the mole fraction of inert and plug it into POLYMATH and change the inert value from 0 to .9 record the results. To determine final conversion use the POLYMATH program given in the example and make F_{A0} a function of the mole fraction of the inert and use the equation

$$X = \frac{F_{A0} - F_A}{F_{A0}}$$

to find the conversion. Record the results and graph the two conversions as a function of mole fraction:



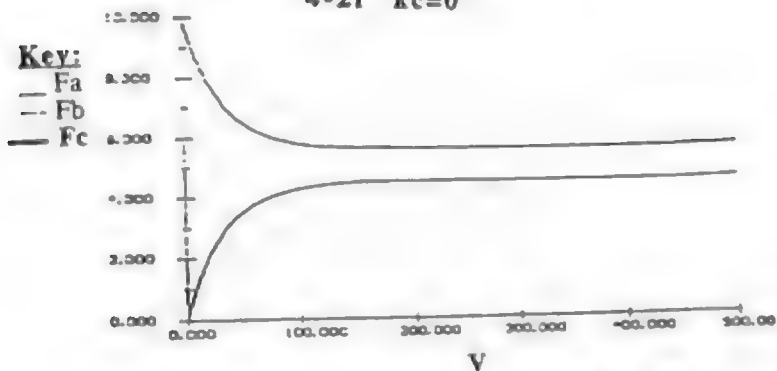
The advantages of the inert are obvious by the graph; as more inert is added the conversion increases. The disadvantage is that the more inert you add the less of A you will have and thus the less of B you will create.

(f) The following graphs show the flow rates of A, B, and C as a function of volume. Each graph represents a different k_c value.

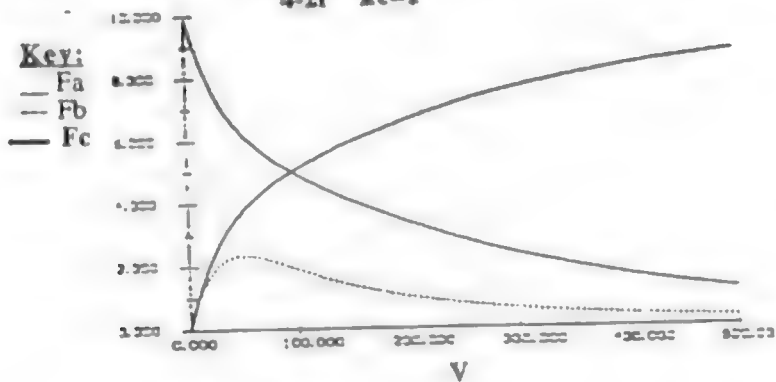
For k_c values not shown it should be noted that as k_c increases, the maximum value of F_B decreases, while the other flow rates are mostly unaffected.

4-2 cont'd

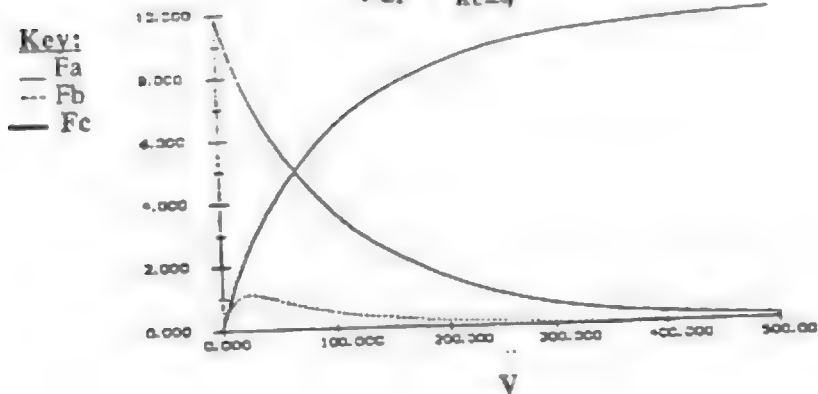
4-2f $kc=0$



4-2f $kc=1$



4-2f $kc=4$

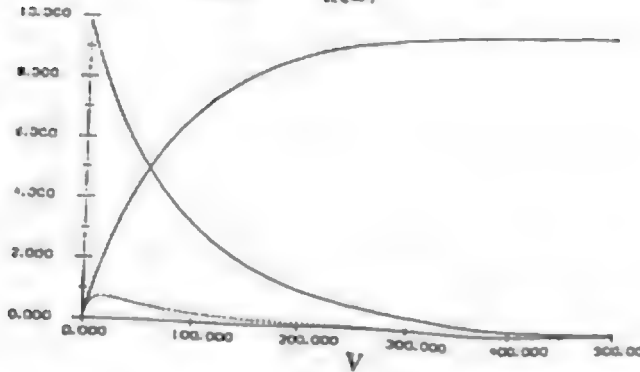


4-2 cont'd

4-2f

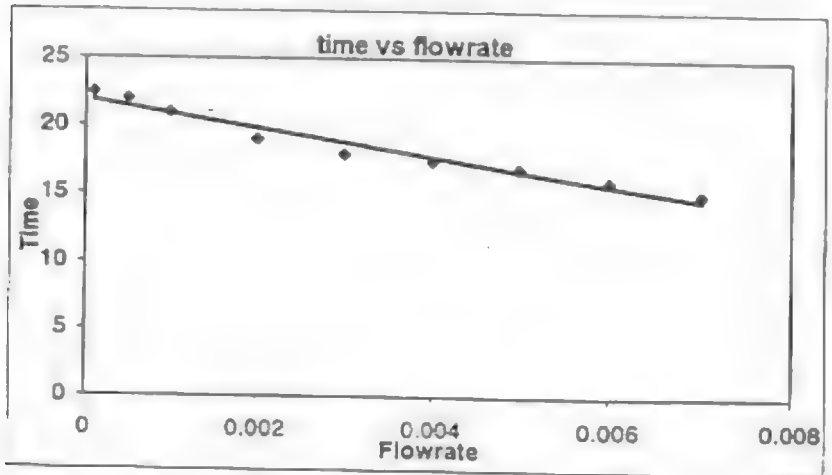
$k_c = 7$

Key:
— F_a
— F_b
— F_c



By varying the parameters, k, k_c, K_c, F_{A0} , it can be determined that keeping the k to k_c ratio high would optimize the process getting the reaction done in less volume. K_c has little effect on the reaction as a whole. Keeping F_{A0} low also helps keep the volume down, but on the other hand it keeps it from having too much reacted. If the temperature were raised the volume needed would decrease.

g)



P4-2 cont'd

The maximum concentration of C and D in Example 4-22 is the derivative of C_A set to equal zero.

$$\frac{dC_C}{dt} = kC_A C_B - \frac{v_0 C_C}{V} = 0$$

$$\frac{dC_D}{dt} = kC_A C_B - \frac{v_0 C_D}{V} = 0$$

h) If one substitutes the numbers

$$\begin{aligned} \text{profit} &= \left[.150 \frac{\text{lb mol}}{\text{s}} \cdot 44.04 \cdot 3600 \cdot 24 \cdot 365 \cdot .6 \right] - \\ &[0.04 \cdot .425 \cdot 30.06 \cdot 3600 \cdot 24 \cdot 365] \\ &- [0.043 \cdot 0.0736 \cdot 3600 \cdot 24 \cdot 365] - 8,000,000 = 92 \text{ million} \end{aligned}$$

$$[200,000,000 \cdot 0.38] - ([0.04 \cdot .425 \cdot 30.06] - [0.043 \cdot 0.0736]) \cdot 3600 \cdot 24 \cdot 365 = 52 \text{ million}$$

they will not make as much money

It looks unfavorable. However, ethylene oxide is dangerous to transport and therefore, it will be made at the same location.

i)

$$\tau = \tau_0 + t \qquad \tau_0 = \frac{V_0}{v_0}$$

mole balance goes to :

$$C_{B0} - C_B (1 + k\tau_0) = \tau \frac{dC_B}{d\tau}$$

$$\frac{C_{B0}}{1 + k\tau} - C_B = \frac{\tau}{1 + k\tau_0} \frac{dC_B}{d\tau}$$

$$\frac{1 + k\tau_0}{\tau} d\tau = \frac{dC_B}{\frac{C_{B0}}{1 + k\tau} - C_B}$$

$$1 + k\tau_0 \ln \tau = \ln \frac{\frac{C_{B0}}{1 + k\tau_0}}{\frac{C_{B0}}{1 + k\tau_0} - C_B}$$

$$\ln \tau^{1+k\tau_0} \Big|_{\tau_0}^{\tau} = \ln \frac{\frac{C_{B0}}{1 + k\tau_0}}{\frac{C_{B0}}{1 + k\tau_0} - C_B}$$

$$\ln \left(\frac{\tau_0}{\tau} \right)^{(1+k\tau_0)} = \ln \frac{\frac{C_{B0}}{1 + k\tau_0}}{\frac{C_{B0}}{1 + k\tau_0} - C_B}$$

$$\left(\frac{\tau_0}{\tau}\right)^{(1+k\tau_0)} = \frac{\frac{C_{p0}}{1+k\tau_0}}{\frac{C_{p0}}{1+k\tau_0} - C_s}$$

$$\left(\frac{\tau}{\tau_0}\right)^{-(1+k\tau_0)} = \frac{\frac{C_{p0}}{1+k\tau_0} - C_s}{\frac{C_{p0}}{1+k\tau_0}}$$

$$C_s = \frac{C_{p0}}{1+k\frac{V_0}{v_0}} \left[1 - \left(\frac{V_0 + v_0 t}{V_0} \right) \right]$$

- j) Immediately flush eyes or skin with lots of water for at least 15 minutes while removing contaminated clothing.
- k) Ethylene oxide-Use safety goggles, use butyl rubber gloves. Keep from fire, prevent contact with air.

Bromine cyanide-use in closed system with a vent, use protective clothing and gloves, safety goggles, prevent contact with warm surfaces.

P4-1.	Location	Elevation	Pressure	Boiling Pt.	Time
		km	mm Hg	°C	min
	Ann Arbor	0.21	739	99.2	15
	Boulder	1.630	625	94.6	17
	Carco	3.416	493	88.3	?

Assume reaction is zero order with respect to spaghetti conversion:

$$-r_A = k = A_0 e^{-E/RT} = -\frac{dC_A}{dt}$$

So

$$-C_A \Big|_{C_{A0}}^{C_A} = (A_0 e^{-E/RT})t$$

For complete conversion (i.e.: well cooked) $C_A = 0$ at time t

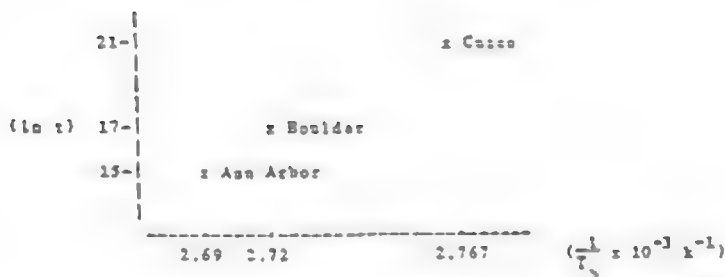
Therefore

$$C_{A0} = A_0 e^{-E/RT}t$$

$$\frac{C_{A0}}{A} = t e^{-E/RT}$$

$$\ln (C_{A0}/A) = \ln k = \ln t - \frac{E}{R} \frac{1}{T_b}$$

→ Can plot the natural log of the cooking time vs. $\frac{1}{T_b}$ and get a linear relationship. Extrapolation to $T_b = 88.3^\circ\text{C} = 361.45 \text{ K}$ yields $t = 21$ minutes



P4-4. Assume constant volume batch reactor.

Mole balance: $C_{A0} \frac{dX}{dt} = -r_A$

Rate law and stoichiometry: $-r_A = kC_A = kC_{A0}(1-X)$

Specific reaction rate: $k(25^\circ\text{C}) = .0022 \text{ weeks}^{-1}$

Combine:

$$t = C_{A0} \int_0^X \frac{dX}{kC_{A0}(1-X)} = \frac{-1}{k} \ln(1-X)$$

$$52.2 \text{ weeks} = \frac{-1}{.0022 \text{ weeks}^{-1}} \ln(1-X)$$

$$X = .108$$

$$C_A = C_{A0}(1-X)$$

Since, volume and molecular weight are constant the equation can be rewritten as

$$m_A = m_{A0}(1-X)$$

$$6500 \text{ IU} = m_{A0}(1-0.108)$$

$$m_{A0} = 7287 \text{ IU}$$

$$\%OU = \frac{C(t=0) - C(t=1 \text{ yr})}{C(t=1 \text{ yr})} \times 100 = 12.1\%$$

4-14

P4-4 (cont'd)

b) Serving size = 30 g. 10,000,000 lbs/year (4.58×10^9 g/year) of cereal made.

$$\text{Number of servings per year} = (4.58 \times 10^9) / 30 = 1.51 \times 10^8$$

Each serving uses excess of 787 IU (1.02×10^6 lb) of nutrients.

$$\text{Total excess per year} = (1.51 \times 10^8) \cdot (1.02 \times 10^6) = 154.11 \text{ lb/year}$$

$$\text{Total overuse cost} = \$5/\text{lb} \cdot 154.11 \text{ lb/year} = \$770.60/\text{year}$$

c) If the nutrients are too expensive, it could be more economical to store the cereal at lower temperatures where nutrients degrade more slowly, therefore lowering the amount of overuse. The cost of this storage could prove to be the more expensive alternative. A cost analysis needs to be done to determine which situation would be optimal

d) $k(40^\circ\text{C}) = 0.0048 \text{ weeks}^{-1}$

6 months = 26 weeks

$$t = C_{A0} \int_0^X \frac{dX}{k C_{A0} (1-X)} = \frac{-1}{k} \ln(1-X)$$

$$26 \text{ weeks} = \frac{-1}{0.0048 \text{ weeks}^{-1}} \ln(1-X)$$

$$X = 0.12$$

$$C_A = C_{A0}(1-X)$$

Since, volume and molecular weight are constant the equation can be rewritten as

$$m_A = m_{A0}(1-X)$$

$$6500 \text{ IU} = m_{A0}(1-0.108)$$

$$m_{A0} = 7367.12 \text{ IU}$$

$$\% \text{OU} = \frac{C(t=0) - C(t=1/2 \text{ yr})}{C(t=1/2 \text{ yr})} \times 100 = 13.34\%$$

4-15

P4-5.



$$C_{A0} = C_{B0} = 2 \text{ mol/dm}^3 \quad k_1 = 0.07 \text{ dm}^3/\text{mol}\cdot\text{min}$$

$$v_A = v_B = 5 \text{ dm}^3/\text{min} \quad E_A = 20,000 \text{ cal/mol}$$

$$T_1 = 300\text{K}$$

$$\text{Rate Law: } r_A = -kC_A C_B$$

$$C_A = C_{A0}(1-X)$$

$$C_j = F_{j0}/v_j$$

a) CSTR

$$V = 200 \text{ dm}^3 \quad T = 350 \text{ K}$$

Using the Arrhenius equation at the CSTR temperature of 350K yields the new specific reaction rate.

$$k = 0.07 \exp \frac{20,000}{1.987} \left(\frac{1}{300} - \frac{1}{350} \right)$$

$$k = 8.45 \text{ dm}^3/\text{mol}\cdot\text{min}$$

$$\text{CSTR Design Equation: } X = (V)(-r_A)/(F_{A0})$$

$$X = \frac{(200 \text{ dm}^3) \left(8.45 \frac{\text{dm}^3}{\text{mol}\cdot\text{min}} \right) \left(1 \frac{\text{mol}}{\text{dm}^3} \right)^2 (1-X)^2}{10 \frac{\text{mol}}{\text{min}}}$$

$$\text{From the quadratic equation: } X = 0.925$$

$$\text{PFR } V = 800 \text{ dm}^3$$

$$T = 300\text{K}$$

Design Equation:

$$F_{A0} \frac{dX}{dV} = -r_A$$

$$dX = \frac{\left(0.07 \frac{\text{dm}^3}{\text{mol}\cdot\text{min}} \right) \left(1 \frac{\text{mol}}{\text{dm}^3} \right)^2 (1-X)^2}{10 \frac{\text{mol}}{\text{min}}} dV$$

$$\int_0^X \frac{dX}{(1-X)^2} = 0.007 \int_0^{800} dV$$

$$X = 0.85$$

P4-5 (cont'd)

b) Batch Reactor $V=200\text{dm}^3$ $N_{A0}=N_{B0}=200$ moles $X=0.90$ Assume Isothermal

Design Equation:

$$t = N_{A0} \int_0^X \frac{dX}{-r_A V}$$

$$t = \frac{(200 \text{ moles})}{\left(8.45 \frac{\text{dm}^3}{\text{mol} \cdot \text{min}}\right) \left(1 \frac{\text{mol}}{\text{dm}^3}\right)^2 (200 \text{ dm}^3)} \int_0^{0.9} \frac{dX}{(1-X)^2}$$

$$t = 1.06 \text{ min}$$

c) $T=273$ K

Find the specific reaction rate at the new temperature of 273 K using the Arrhenius Equation.

$$k = 2.54 \times 10^{-3}$$

$$t = \frac{(200)(9)}{(2.54 \times 10^{-3})(200)} = 3543 \text{ min} = 2.5 \text{ days}$$

d) At higher temperatures the rate of the reaction may be extremely high. If the reaction is extremely exothermic, the temperature in the reactor may get too high making the process unsafe.

e) Assume for each batch it takes three hours to fill, empty, clean, and heat to the reaction temperature. The reaction takes one minute to complete, therefore we can carry out eight batches a day.

In one day, the reactor processes: $(10 \text{ mol/min})(60 \text{ min/hr})(24 \text{ hr/day}) = 1800 \text{ mol/batch}$

$$C_{A0} = \frac{1 \text{ mol}}{\text{dm}^3} = \frac{N_{A0}}{V} = \frac{1800 \text{ mol}}{V}$$

$$V = 1800 \text{ dm}^3$$

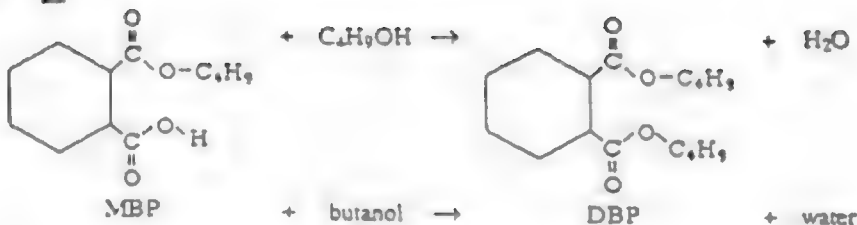
Use a 500 gallon reactor at a cost of \$67,000. (1997 prices)

f) The points of the problem are:

- (1) To note the significant differences in processing times at different temperatures (i.e. compare part (b) and (c).)
- (2) That the reaction is so fast at 77°C that a batch reactor is not appropriate. One minute to react and 180 to fill and empty.
- (3) Not to be confused by irrelevant information. It does not matter if the reactor is red or black.

4-17

24-8. b)



Species	Symbol	Entering	Change	Leaving
MBP	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
butanol	B	$5F_{A0}$	$-F_{A0}X$	$F_B = F_{A0}(5-X)$
DBP	C	0	$F_{A0}X$	$F_C = F_{A0}X$
water	D	0	$F_{A0}X$	$F_D = F_{A0}X$

entering $F_{\text{butanol}} = 5 F_{\text{MBP},0}$

$$-r_A = k C_A C_B$$

$$-r_A = k (F_A/v) (F_B/v)$$

elementary reaction

for liquid systems

volumetric flow $v = v_0$

$$-r_A = k C_{A0}^2 (1-X)(5-X)$$

$$V_{\text{CSTR}} = \frac{F_{A0}X}{-r_A} = \frac{F_C}{k C_{A0}^2 (1-X)(5-X)}$$

$$\dot{m}_C = 4 \times 10^6 \frac{\text{lb}}{\text{yr}}, F_C = 4 \times 10^6 \text{ lb/yr}, 30\text{d/yr operation}$$

$$F_C = 4 \times 10^6 \frac{\text{lb}}{\text{yr}} \times \frac{1 \text{ yr}}{30\text{d}} \times \frac{1 \text{ d}}{24 \text{ hr}} \times \frac{1 \text{ lb mol}}{278 \text{ lb}} = 20.0 \frac{\text{mol}}{\text{hr}}$$

$$V_{\text{CSTR}} = 1000 \text{ gal} \times \frac{1 \text{ ft}^3}{7.48 \text{ gal}} = 133.7 \text{ ft}^3$$

$$133.7 \text{ ft}^3 = \frac{20 \text{ lbmole/hr}}{1.2 \frac{\text{ft}^3}{\text{lbmole} \cdot \text{hr}} \left(\frac{0.2 \text{ lbmole}}{\text{ft}^3} \right)^2 (1-X)(5-X)}$$

$$X^2 - 6X + 1.89 = 0$$

$$X = 0.33$$

b) To increase conversion, X, use PFR, higher temperature, θ_B , or use a better catalyst.

4-18

(c)

$$\text{MB} \quad V = \frac{F_{A0}X}{-r_A}$$

$$\text{RL} \quad -r_A = kC_A C_B$$

$$\text{S} \quad C_A = C_{A0}(1-X) \quad F_{A0} = \frac{1 \text{ lbmol}}{\text{min}} = \frac{60 \text{ lbmol}}{\text{hr}}$$

$$C_B = C_{A0}(5-X)$$

$$\text{C} \quad V = \frac{F_{A0}X}{kC_{A0}^2(1-X)(5-X)}$$

$$\text{E} \quad V = \frac{(60 \text{ lbmol/h})(85)}{\left(\frac{1.2 \text{ ft}^3}{\text{lbmol} \cdot \text{h}}\right) \left(\frac{0.2 \text{ lbmol}}{\text{ft}^3}\right)^2 (1-.85)(5-.85)}$$

d) PFR Design Equation

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

$$\frac{dX}{dV} = \frac{kC_{A0}^2(1-X)(5-X)}{F_{A0}}$$

$$V = 535 \text{ dm}^3$$

$$\text{e) } M_w(\text{DBP}) = 278 \text{ lb/lbmol} \quad V = 1000 \text{ gal} = 133.7 \text{ ft}^3$$

therefore $14.4 \times 10^3 \text{ lbmol}$ of DBP need to be produced in 30 days

$$\begin{aligned} \text{Mole balance:} \quad t &= N_{A0} \int_0^X \frac{dX}{-r_A V} \\ t &= \frac{1}{kC_{A0}} \frac{1}{(5-1)} \ln\left(\frac{5-X}{5(1-X)}\right) \end{aligned}$$

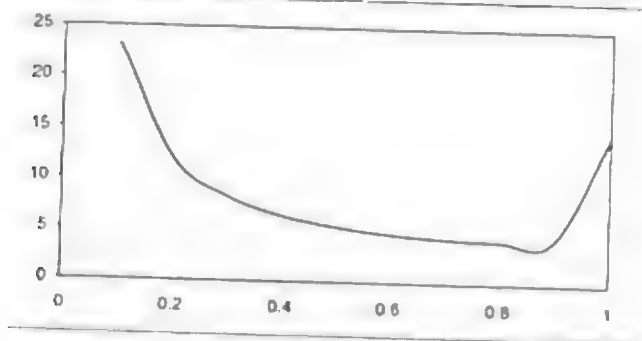
The above equation relates the reaction time for a batch and the conversion achieved during that batch. There is a trade-off between high conversion and few batches and low conversion but many batches per day. What conversion will result in the smallest number of reactors?

$$\begin{aligned} N_{A0} &= 133.7 \text{ ft}^3 \cdot C_{A0} & C_{A0} &= 0.2 \text{ lbmol / ft}^3 \\ \frac{\text{Product}}{\text{reactor} \cdot \text{day}} &= \frac{N_{A0}X \cdot 24 \text{ hr}}{t_{\text{batch}}} = \frac{N_{A0}X \cdot 24}{t_{\text{res}} + 3} = \frac{N_{A0}X \cdot 24}{\frac{1}{kC_{A0}} \ln\left(\frac{5-X}{5(1-X)}\right) + 3} = f(X) \end{aligned}$$

$$\frac{\text{Mole product}}{\text{day}} = \frac{4 \cdot 10^6 \text{ lbs lbmol}}{30 \text{ days } 278 \text{ lb}} = 480 \frac{\text{mol}}{\text{day}}$$

$$n = \frac{480 \text{ mol / day}}{f(X) \text{ mol / day / reactor}}$$

P4-6 (cont'd)



The minimum occurs at $X = 0.82$ and corresponds to 4.192 or 5 reactors

P4-7 (a)



$$V = \frac{F_{A0}X}{-r_A}$$

$$-r_A = kC_A$$

$$C_A = C_{A0} \frac{(1-X)}{(1+\epsilon X)} \quad \epsilon = y_{A1}\delta = (1)(2+1-1) = 2$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{10}{(0.082)(400)} = 0.3 \frac{\text{mol}}{\text{dm}^3}$$

$$V = \frac{F_{A0}X(1+\epsilon X)}{C_{A0}k(1-X)}$$

$$k = 10^{-4} \frac{85,000 \left(\frac{1}{32} - \frac{1}{400} \right)}{\text{dm}^3} = 0.044$$

$$V = \frac{(2.5 \text{ mol/min})(0.9)(1+2(0.9))}{(0.044 \text{ min}^{-1})(0.3 \text{ mol/dm}^3)(1-0.9)} = 4772 \text{ dm}^3$$

(b)

$$V = F_{A0} \int_0^X \frac{dX}{-r_A} = \frac{F_{A0}}{kC_{A0}} \int_0^X \frac{(1+\epsilon X)}{(1-X)} dX$$

$$= \frac{F_{A0}}{kC_{A0}} \left[(1+\epsilon) \ln \frac{1}{1-X} - \epsilon X \right]$$

$$= \left(\frac{(2.5 \text{ mol/min})}{(0.044 \text{ min}^{-1})(0.3 \text{ mol/dm}^3)} \right) \left((1+2) \ln \frac{1}{1-0.9} - 1.8 \right)$$

$$= (159.4 \text{ dm}^3)(5.11)$$

$$V = 967 \text{ dm}^3$$

P4-7 (cont'd)



Rate Law: $-r_A = -k_f(C_A - C_B C_C^2 / K_C) = 0$ (at equilibrium)

$K_C = 0.025$

Stoichiometry: $C_A = \frac{C_{A0}(1-X)}{1+\epsilon X}$, $C_B = \frac{C_{A0}X}{1+\epsilon X}$, $C_C = \frac{2C_{A0}X}{1+\epsilon X}$

$K_C = \frac{C_B C_C^2}{C_A} = \left(\frac{C_{A0}X}{1+\epsilon X} \right) \left(\frac{2C_{A0}X}{1+\epsilon X} \right)^2 \left(\frac{1+\epsilon X}{C_{A0}(1-X)} \right) = \frac{4C_{A0}^3 X^3}{(1+\epsilon X)^2 (1-X)}$

$\epsilon = 2$ and $C_{A0} = 0.3$

$X_{eq} = 0.52$

$X = (0.90)X_{eq} = 0.47$

CSTR

$-r_A = \frac{kC_{A0}}{(1+\epsilon X)} \left((1-X) - \frac{4C_{A0}^3 X^3}{(1+\epsilon X)^2 K_C} \right)$

$V = \frac{F_{A0}X(1+\epsilon X)}{kC_{A0} \left((1-X) - \frac{4C_{A0}^3 X^3}{(1+\epsilon X)^2 K_C} \right)} = \frac{(2.5 \text{ mol/min})(0.47)(1+2(0.47))}{(0.044 \text{ min}^{-1})(0.3 \text{ mol/dm}^3) \left((1-0.47) - \frac{4(0.3 \text{ mol/dm}^3)^3 (0.47)^3}{(1+2(0.47))^2 (0.025)} \right)}$

$V = 1300 \text{ dm}^3$

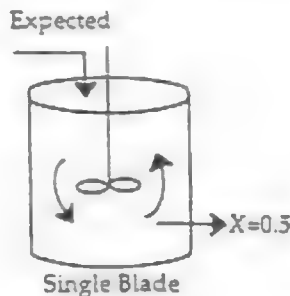
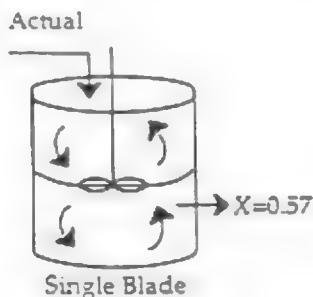
PFR

$F_{A0} \frac{dX}{dV} = -r_A$ or $\frac{dV}{dX} = \frac{F_{A0}}{-r_A}$

$-r_A = \frac{kC_{A0}}{(1+\epsilon X)} \left((1-X) - \frac{4C_{A0}^3 X^3}{(1+\epsilon X)^2 K_C} \right)$

Using these equations in the POLYMATH program below we get the volume to be 290 dm^3 .

P4-8



$$c) \quad t = C_{A0} \int_0^X \frac{dX}{-r_A} = \frac{1}{0.044 \text{ min}^{-1}} \int_0^X \frac{1+2X}{1-X} dX = 116 \text{ min}$$

It takes 116 min for the reaction to reach 90% conversion in the batch reactor. Assume that down time (table 4-1) is six hours (360 min).

Therefore, total cycle time = 116 min + 360 min = 476 min

In one day there are 1440/476 = 3.03 = 3 runs

Therefore $N_{A0} = 3600/3 = 1200$ moles

Volume Calculations:

$$t = \frac{N_{A0}}{V} \int_0^X \frac{dX}{-r_A} =$$

$$116 \text{ min} = \frac{1200 \text{ mole}}{V \cdot 0.044 \text{ min}^{-1} \cdot 3} \int_0^X \frac{1+2X}{1-X} dX$$

$$V = 4000 \text{ dm}^3$$



Rate Law: $-r_A = -k_f(C_A - C_B C_C^2 / K_C) = 0$ (at equilibrium)

$$K_C = 0.025$$

$$\text{Stoichiometry: } C_A = \frac{C_{A0}(1-X)}{1+\epsilon X}, \quad C_B = \frac{C_{A0}X}{1+\epsilon X}, \quad C_C = \frac{2C_{A0}X}{1+\epsilon X}$$

$$K_C = \frac{C_B C_C^2}{C_A} = \left(\frac{C_{A0}X}{1+\epsilon X} \right) \left(\frac{2C_{A0}X}{1+\epsilon X} \right)^2 \left(\frac{1+\epsilon X}{C_{A0}(1-X)} \right) = \frac{4C_{A0}^3 X^3}{(1+\epsilon X)^2 (1-X)}$$

$$\epsilon = 2 \text{ and } C_{A0} = 0.3$$

$$X_{eq} = 0.52$$

$$X = (0.90)X_{eq} = 0.47$$

CSTR

$$-r_A = \frac{k C_{A0}}{(1+\epsilon X)} \left((1-X) - \frac{4C_{A0}^3 X^3}{(1+\epsilon X)^2 K_C} \right)$$

$$V = \frac{F_{A0} X (1+\epsilon X)}{k C_{A0} \left((1-X) - \frac{4C_{A0}^3 X^3}{(1+\epsilon X)^2 K_C} \right)} = \frac{(2.5 \text{ mol/min})(0.47)(1+2(0.47))}{(0.044 \text{ min}^{-1})(0.3 \text{ mol/dm}^3) \left((1-0.47) - \frac{4(0.3 \text{ mol/dm}^3)^3 (0.47)^3}{(1+2(0.47))^2 \cdot 0.025} \right)}$$

$$V = 1300 \text{ dm}^3$$

Predicted

$$V = \frac{F_{A0}X(1+\varepsilon X)}{C_{A0}^2 k(1-X)^2} = a \frac{X}{(1-X)^2}$$

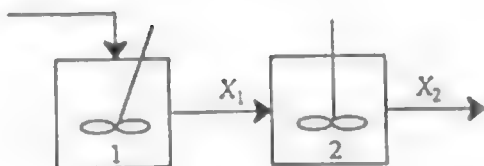
$$[a] = \frac{F_{A0}}{C_{A0}^2 k} = \frac{\frac{\text{mol}}{\text{min}}}{\frac{\text{gal}}{\text{mol min}} \left(\frac{\text{mol}}{\text{gal}} \right)^2}$$

$$a = [\text{gal}]$$

$$1000 \text{ gal} = a \frac{X}{(1-X)^2} = a \frac{.5}{.25} = 2a$$

$$a = 500 \text{ gal}$$

Measured



$$V = a \frac{X}{(1-X)^2} \text{ For Reactor 1}$$

$$500 \text{ gal} = \frac{500 \text{ gal } X_1}{(1-X_1)^2}$$

$$1 - 2X_1 + X_1^2 = X$$

$$1 - 3X_1 + X_1^2 = 0$$

$$X_1 = \frac{3 \pm \sqrt{9-4}}{2} = .38$$

Reactor 2

$$500 = \frac{500 (X_2 - .38)}{(1-X_2)^2}$$

$$1 - 2X_2 + X_2^2 = X_2 - .38$$

$$X_2^2 - 3X_2 + 1.38 = 0$$

$$X_2 = \frac{3 \pm \sqrt{9-4(1.38)}}{2} = .57$$

4-23

P4-10

(a) Benzene is A

$$-r_A = k_A \left(C_A^2 - \frac{C_B C_C}{K_C} \right)$$

for equilibrium $-r_A = 0 \quad \therefore \quad C_A^2 - \frac{C_B C_C}{K_C} = 0$

$$C_A^2 = \frac{C_B C_C}{K_C}$$

$$C_A = C_{A0}(1-X) \quad C_B = \frac{C_{A0}X}{2} \quad C_C = \frac{C_{A0}X}{2}$$

$$C_{A0}^2 (1-X_c)^2 = \frac{C_{A0}^2 X_c^2}{4K_c}$$

$$4K_c (1-X_c)^2 = X_c^2$$

$$4K_c - 8K_c X_c + 4K_c X_c^2 = X_c^2$$

$$0.2X^2 - 2.4X_c + 1.2 = 0$$

$$X_c = 0.52$$

(b) PFR

Design Equation: $V = F_{A0} \int \frac{dX}{-r_A}$

Rate Law: $-r_A = k_A \left(C_A^2 - \frac{C_B C_C}{K_C} \right)$

Stoichiometry: $C_A = C_{A0}(1-X) \quad C_B = \frac{C_{A0}X}{2} \quad C_C = \frac{C_{A0}X}{2}$

$$C_{A0} = \frac{P}{RT} = \frac{5 \text{ atm}}{\left(0.73 \frac{\text{ft}^3 \cdot \text{atm}}{\text{lbmol} \cdot ^\circ \text{R}} \right) (1859.67^\circ \text{R})} = 0.0037 \frac{\text{lbmol}}{\text{ft}^3}$$

4-24

P4-10 (cont'd)

Combine :

$$V = \frac{F_{A0}}{kC_{A0}^2} \int_0^x \frac{dX}{\left[(1-X)^2 - \frac{X^2}{4K_c} \right]}$$

$$V = \frac{(10 \text{ lbmol/min})(1 \text{ min}/60 \text{ s})}{(1800 \text{ ft}^3/\text{lbmol} \cdot \text{s})(0.0037)^2} \int_0^x \frac{dX}{\left[(1-X)^2 - 0.833X^2 \right]}$$

$$V = 6.76 \text{ ft}^3 \int_0^x \frac{dX}{\left[1 - 2X + 0.167X^2 \right]}$$

$$V = 6.76 \left(\frac{1}{(0.617)(1.45 - 0.523)} \ln \left[\frac{0.523 \left(\frac{X - 1.45}{X - 0.523} \right) \right] \right)$$

$$V = 13.5 \text{ ft}^3$$

(c) CSTR

Design Equation : $V = \frac{F_{A0}X}{-r_A}$

Rate Law : $-r_A = k_A \left(C_A^2 - \frac{C_B C_C}{K_c} \right)$

Stoichiometry : $C_A = C_{A0}(1-X) \quad C_B = \frac{C_{A0}X}{2} \quad C_C = \frac{C_{A0}X}{2}$

Combine : $V = \frac{F_{A0}X}{k_A C_{A0}^2 \left[(1-X)^2 - \left(\frac{X^2}{4K_c} \right) \right]}$

$$V = \frac{(10)(0.51)(1/60)}{(1800)(0.0037)^2 \left[(1-0.51)^2 - \left(\frac{0.51^2}{4(0.3)} \right) \right]} = 147.73 \text{ ft}^3$$

(d)

Amount processed in CSTR :

$$(10 \text{ lbmol/min})(60 \text{ min/hr})(24 \text{ hr/day}) = 14,400 \text{ lbmol/day}$$

4-25

P4-10 (cont'd)

Batch

$$t = C_{A0} \int \frac{dX}{-r_A} = \frac{C_{A0}}{kC_{A0}^2} \int \frac{dX}{\left[(1-X)^2 - \frac{X^2}{4K_t}\right]}$$

$$t = \frac{1}{kC_{A0}} \left(\frac{1}{(0.167)(11.45 - 0.523)} \ln \left[\frac{0.523 \left(\frac{X - 11.45}{X - 0.523} \right) \right] \right)$$

$$t = 0.30 \text{ s}$$

Taking into account the time it takes to clean the reactor and other down time assume that the total time per run is 4 hours. Assuming that the reactor can be used twenty-four hours a day there can be 6 runs per day.

$$\frac{14,400 \text{ lbmol/day}}{6 \text{ runs/day}} = 2400 \text{ lbmol/run}$$

$$t = \frac{N_{A0}}{V} \int \frac{dX}{-r_A} \quad \therefore \quad V = \frac{N_{A0}}{t} \int \frac{dX}{-r_A}$$

$$V = \frac{N_{A0}}{t} \frac{1}{kC_{A0}^2} \left(\frac{1}{(0.167)(11.45 - 0.523)} \ln \left[\frac{0.523 \left(\frac{X - 11.45}{X - 0.523} \right) \right] \right)$$

$$V = \frac{2400}{(4)(1800)(0.0037)^2} \left(\frac{1}{(0.167)(11.45 - 0.523)} \ln \left[\frac{0.523 \left(\frac{X - 11.45}{X - 0.523} \right) \right] \right)$$

$$V = 48,690 \text{ ft}^3$$

(c) $E = 30,202 \text{ btu/lbmol}$

for $X = 0$, $-r_A = kC_{A0}^2$

$$\frac{-r_{A(800)}}{-r_{A(1400)}} = \frac{k_{800}C_{A0}^2}{k_{1400}C_{A0}^2} = \frac{k_{800}}{k_{1400}} = \exp \frac{E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\frac{-r_{A(800)}}{-r_{A(1400)}} = \exp \frac{30,202 \text{ btu/lbmol}}{1.987 \text{ btu/lbmol} \cdot ^\circ\text{R}} \left(\frac{1}{1259.67^\circ\text{R}} - \frac{1}{1859.67^\circ\text{R}} \right)$$

$$\frac{-r_{A(800)}}{-r_{A(1400)}} = 49$$

$$\frac{-r_{A(800)}}{-r_{A(1400)}}$$

P4-11.

Given: Gaseous reaction in a tubular reactor:



$$E = 25,000 \text{ cal/gmole}$$



$$X = 0.90$$

$$W_B = 1000 \text{ lb/hr}$$

$$(M)_{\text{A}} = 58 \text{ lb/lb-mole}$$

$$(MW)_{\text{B}} = 58 \text{ lb/lb-mole}$$

$$D_t = \text{tube diameter} = 1 \text{ inch (I.D.)}$$

$$L = \text{tube length} = 10 \text{ feet}$$

$$P = 132 \text{ psig} = (132 + 14.7) \text{ psia} = 146.7 \text{ psia}$$

$$T = 260^\circ\text{F} = 720^\circ\text{R}$$

$$n_t = \text{number of tubes}$$

$$F_B = \frac{1000 \text{ lb/hr}}{58 \text{ lb/lb-mole}} = 17.21 \frac{\text{lb-mole}}{\text{hr}} : F_{\text{AO}} = \frac{F_B}{X} = (17.21 \text{ lb-mole/hr}) / 0.9 = 19.1 \text{ lb-mole/hr.}$$

$$\text{For a plug flow reactor: } V = \frac{n_t P D_t^2 L}{4} = F_{\text{AO}} \int_0^{0.90} \frac{dX}{-r_A}$$

$$\delta = 1 - 1 = 0 \quad \gamma_A = 1.0 \quad \epsilon = \gamma_A \delta = 0$$

$$\therefore -r_A = k C_{\text{AO}} (1 - X) \quad C_{\text{AO}} = \frac{P_A}{RT} = \frac{P}{RT}$$

$$\therefore V = F_{\text{AO}} \int_0^{0.90} \frac{dX}{-r_A} = F_{\text{AO}} \int_0^{0.90} \frac{dX}{k C_{\text{AO}} (1 - X)} = \frac{F_{\text{AO}}}{k C_{\text{AO}}} \ln \frac{1}{1 - 0.90} = \frac{F_{\text{AO}} RT}{k P} \ln 10$$

$$\text{At } T_2 = 260^\circ\text{F} = 720^\circ\text{R, with } k_1 = .0015 \text{ min}^{-1} \text{ at } T_1 = 80^\circ\text{F} = 540^\circ\text{R.}$$

$$k_2 = k_1 \exp\left(\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) =$$

P4-11 (cont'd)

$$.0015 \exp \left\{ \frac{\frac{25,000 \text{ cal}}{\text{gmole}}}{\frac{1.99 \text{ BTU}}{\text{lbmole}^\circ\text{R}}} \left(\frac{1}{540^\circ\text{R}} - \frac{1}{720^\circ\text{R}} \right) + \frac{1.8 \text{ BTU}}{\text{lbmole}} \cdot \frac{\text{cal}}{\text{gmole}} \right\}$$

$$k_2 = .0015 \text{ min}^{-1} \exp \left\{ \left[\frac{25,000}{1.99} \right] \left(\frac{180(1.8)}{(540)(720)} \right) \right\} = .0015 e^{10.487} \text{ min}^{-1}$$

$$k_2 = (.0015) (3.52 \times 10^4) \text{ min}^{-1} = 52.8 \text{ min}^{-1}$$

$$\therefore V = \left(\frac{19.1 \text{ lbmole/s}}{\text{hr}} \right) \left(\frac{1 \text{ min}}{52.8} \right) \left(\frac{1 \text{ hr}}{60 \text{ min}} \right) \left[\frac{10.73 \text{ ft}^3}{\text{lbmole}^\circ\text{R} \text{ psia} \times 720^\circ\text{R}} \right] \ln 10$$

$$= 0.73 \text{ ft}^3$$

$$V = \frac{n_t \pi D_t^2 L}{4} ; \therefore n_t = \frac{4V}{\pi D_t^2 L} = \frac{(4)(0.73) \text{ ft}^3}{3.14 (1/12)^2 \text{ ft}^2 (10) \text{ ft}} = 13.4$$

$$\therefore n_t = 14 \text{ pipes}$$

P4-12. Given: Tubular flow reactor:

$$F_{AO} = F_{CO}$$

$$F_{BO} = 0$$



Case 1:

Rearrange reaction: $A \rightarrow \frac{1}{2} B$ Then: $\delta = \frac{1}{2} - 1 = -1/2$

$$\theta_B = 0 ; \theta_C = 1 ; y_{AO} = \frac{F_{AO}}{F_{AO} + F_{BO} + F_{CO}} = \frac{1}{2} ; z = y_{AO} \delta = -1/4$$

For a plug flow reactor:

$$V_{PF} = F_{AO} \int_0^1 \frac{dX}{-r_A} ; -r_A = k C_A^2 = \frac{k C_{AO}^2 (1-X)^2}{(1+zX)^2}$$

P4-12 (cont'd)

$$\therefore \frac{k C_{AO}^2 v_{PF}}{F_{AO}} = \frac{v_{PF} P^2}{4 F_{AO} R^2 T^2} \quad \text{and} \quad \frac{k C_{AO}^2 v_{PF}}{F_{AO}'} = \frac{v_{PF} P^2}{9 F_{AO} R^2 T^2}$$

$$\therefore \frac{k C_{AO}^2 v_{PF}}{F_{AO}'} = \frac{8}{9} \times \frac{k C_{AO}^2 v_{PF}}{F_{AO}} = \frac{8}{9} = (2.90) = 2.58$$

$$\therefore 2.58 = e^{X'} + 2e^{X'}(1+e^{X'}) \ln(1-X') + \frac{(e^{X'}+1)^2 X'}{(1-X')} \quad \text{(last term be)}$$

solved by trial and error. Dominating term is underlined. Rearranging the above equation

$$X' = \left(\frac{[2.58 - e^{X'} - 2e^{X'}(1+e^{X'}) \ln(1-X')]}{(1+e^{X'})^2 + [2.58 - e^{X'} - 2e^{X'}(1+e^{X'}) \ln(1-X')]} \right)$$

Solution (1) Assume a value of X'

(2) Calculate a new X' from L.H.S. of the above equation

(3) Compare or use new value of X' in L.H.S. of the equation and repeat steps (2) and (3).

$$X' = \frac{2.58 - 0.0278X' + 0.278 \ln(1-X')}{3.27 - 0.0278X' + 0.278 \ln(1-X')}$$

X' Assumed	X' Calculated	% Difference
0.700	0.763	9.0%
0.763	0.758	0.7%
0.758	0.758	----

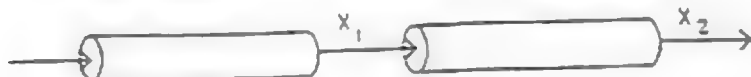
$$\therefore X = 0.758$$

P4-13. Given: The metal catalyzed isomerization, $A \xrightarrow{\text{---}} B$, liquid phase

$$-r_A = k_1 [C_A - C_B/K_{eq}] \quad \text{with } K_{eq} = 5.6$$

For a plug flow reactor with $y_A = 1.0$, $X_1 = 0.55$

Case I: P.F. reactor connected in series with that described above



P4-13 (cont'd)

Since $r_A = 1.0$, $\theta_B = 0$ For a liquid phase reaction, $C_A = C_{A0}(1-X)$.

$$C_B = C_{A0}X; \quad -r_A = k C_{A0} \left[(1-X) - \frac{X}{K_{eq}} \right]$$

For the first reactor,

$$V_1 = F_{A0} \int_0^{X_1} \frac{dX}{-r_A} = F_{A0} \int_0^{X_1} \frac{dX}{k C_{A0} [(1-X) - X/K_{eq}]} \quad \text{or}$$

$$\frac{k C_{A0} V_1}{F_{A0}} = \int_0^{X_1} \frac{dX}{1 - (1 + 1/K_{eq})X} = - \frac{1}{(1 + 1/K_{eq})} \ln \left[1 - \left(1 + \frac{1}{K_{eq}} \right) X \right] \Big|_0^{X_1}$$

$$\frac{k C_{A0} V_1}{F_{A0}} = - \frac{1}{\left(1 + \frac{1}{K_{eq}} \right)} \ln \left[1 - \left(1 + \frac{1}{K_{eq}} \right) X_1 \right] \quad (a)$$

For the second reactor $V_2 = F_{A0} \int_{X_1}^{X_2} \frac{dX}{-r_A}$ or upon rearrangement

$$\frac{k C_{A0} V_2}{F_{A0}} = \int_{X_1}^{X_2} \frac{dX}{[1 - (1 + \frac{1}{K_{eq}})X]} = - \frac{1}{(1 + 1/K_{eq})} \ln \left[\frac{1 - (1 + \frac{1}{K_{eq}})X_2}{1 - (1 + \frac{1}{K_{eq}})X_1} \right] \quad (b)$$

but $\frac{k C_{A0} V_1}{F_{A0}} = \frac{k C_{A0} V_2}{F_{A0}}$, and thus, from Eqns. (a) and (b)

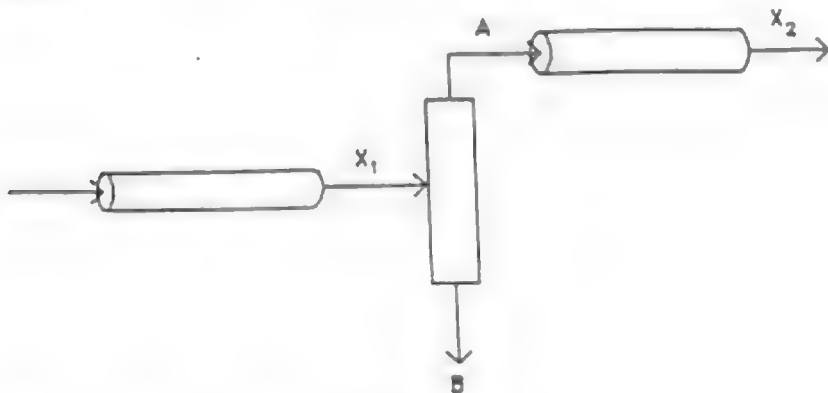
$$- \frac{1}{(1 + 1/K_{eq})} \ln \left[1 - \left(1 + \frac{1}{K_{eq}} \right) X_1 \right] = - \frac{1}{(1 + 1/K_{eq})} \ln \left[\frac{1 - (1 + \frac{1}{K_{eq}})X_2}{1 - (1 + \frac{1}{K_{eq}})X_1} \right]$$

or $1 - \left(1 + \frac{1}{K_{eq}} \right) X_2 = \left[1 - \left(1 + \frac{1}{K_{eq}} \right) X_1 \right]^2$

P4-13 (cont'd)

$$x_2 = \frac{1 - [1 - (1 + \frac{1}{K_{eq}})x_1]^2}{[1 + \frac{1}{K_{eq}}]} = \frac{1 - [1 - (1.173)(.55)]^2}{1.173} = \frac{1 - (.356)^2}{1.173} = .74 \text{ ans}$$

(b) Case II: Product from first reactor separated and pure A sent to second reactor:



Analysis for first reactor same as before

$$\therefore \frac{kC_{AO}V_1}{F_{AO}} = \frac{-1}{(1 + 1/K_{eq})} \ln [1 - (1 + 1/K_{eq})x_1]$$

By material balance on separator, $F_{AO,2} = F_{AO}(1-x_1)$

Since pure A enters second reactor $C_{AO,2} = C_{AO}$, $C_{BO} = 0$, $\theta_2 = 0$

$\therefore C_A = C_{AO}(1-x)$, $C_B = C_{AO}x$ for second reactor

$$V_2 = F_{AO,2} \int_0^{x_2} \frac{dx}{-r_A} = \frac{F_{AO}(1-x_1)}{k C_{AO}} \int_0^{x_2} \frac{dx}{[(1-x) - x/K_{eq}]}$$

$$\therefore \frac{kC_{AO}V_2}{F_{AO}(1-x_1)} = - \frac{1}{(1 + 1/K_{eq})} \ln [1 - (1 + 1/K_{eq})x_2]$$

$$\text{Eut: } \frac{kC_{AO}V_2}{F_{AO}} = \frac{kC_{AO}V_1}{F_{AO}}, \text{ or}$$

P4-13 (cont'd)

$$-\frac{1}{(1+1/K_{eq})} \ln [1 - (1 + \frac{1}{K_{eq}}) X_1] = -\frac{(1-X_1)}{(1+1/K_{eq})} \ln [1 - (1 + \frac{1}{K_{eq}}) X_2]$$

$$1 - (1 + \frac{1}{K_{eq}}) X_2 = [1 - (1 + \frac{1}{K_{eq}}) X_1]^{\frac{1}{1-X_1}}$$

$$X_2 = \frac{1 - [1 - (1 + \frac{1}{K_{eq}}) X_1]^{\frac{1}{1-X_1}}}{1 + \frac{1}{K_{eq}}} = \frac{1 - (1.356)^{-.45}}{1.174} = \frac{1 - .102}{1.174} = 0.766$$

Overall conversion for this scheme:

$$\bar{X} = \frac{F_{AO} - F_{AO,2} (1-X_2)}{F_{AO}} = \frac{F_{AO} - F_{AO} (1-X_1)(1-X_2)}{F_{AO}} = 1 - (1-X_1)(1-X_2) = .89$$

Ans.

P4-14. Given: Ortho to meta and para isomerization of xylene



$$P = 300 \text{ psig}$$

$$T = 750^\circ F$$

$$V = 1000 \text{ ft}^3 \text{ cat.}$$

Assume that reactions are irreversible first order

$$\text{Then: } -r_M = k_1 C_M + k_2 C_M = k C_M; k = k_1 + k_2$$

$$r = 0$$

Check to see what type of reactor is being used

Case I:

$$(V_o)_{\text{Case I}} = 2500 \text{ gal/hr.}; \quad X_{\text{Case I}} = .37$$

Case II:

$$(V_o)_{\text{Case II}} = 1667 \text{ gal/hr.}; \quad X_{\text{Case II}} = .50$$

P4-14 (cont'd)

Assume plug flow reactor conditions: $F_{I0} dI = -r_H dV$ or

$$V = F_{A0} \int_0^X \frac{dX}{-r_H}$$

$$V = \int_0^X \frac{C_{A0} v_0 dX}{-r_H} = v_0 \int_0^X \frac{dX}{k(1-X)} = -\frac{v_0}{k} \ln(1-X)$$

C_{A0} , k and V should be the same for Case I and Case II.

$$\begin{aligned} \therefore (kV)_{\text{Case I}} &= -(v_0)_{\text{Case I}} \ln [1-X_{\text{Case I}}] = -\frac{2500 \text{ gal}}{\text{hr}} \ln (1-.37) \\ &= 1155 \text{ gal/hr.} \end{aligned}$$

$$\begin{aligned} \therefore (kV)_{\text{Case II}} &= -(v_0)_{\text{Case II}} \ln [1-X_{\text{Case II}}] = -\frac{1667 \text{ gal}}{\text{hr}} \ln [1-.50] \\ &= 1155 \text{ gal/hr.} \end{aligned}$$

Reactor appears to be plug flow since $\left(\frac{kV}{C_{A0}}\right)_{\text{Case I}} = \left(\frac{kV}{C_{A0}}\right)_{\text{Case II}}$;

As a check, assume that the reactor behaves as a CSTR:

$$F_{I0} X = C_{A0} v_0 X = (-r_H) V$$

$$\therefore V = \frac{C_{A0} X}{-r_H} v_0 = \frac{v_0 X}{k(1-X)} \text{ or } kV = \frac{v_0 X}{1-X}$$

Again, (kV) should be the same for Case I and Case II:

$$(kV)_{\text{Case I}} = \frac{(v_0)_{\text{Case I}} X_{\text{Case I}}}{1-X_{\text{Case I}}} = \frac{(2500 \text{ gal/hr})(.37)}{1-.37} = 1463 \text{ gal/hr.}$$

$$(kV)_{\text{Case II}} = \frac{(v_0)_{\text{Case II}} X_{\text{Case II}}}{1-X_{\text{Case II}}} = \frac{1667 \text{ gal}}{\text{hr}} = \frac{.50}{1-.50} = 1667 \text{ gal/hr.}$$

$(kV)_{\text{Case I}} = (kV)_{\text{Case II}}$ using the CSTR assumption, reactor can be modeled as a plug flow reactor:

P4-14 (cont'd)

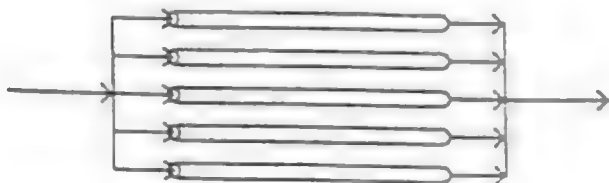
$$\therefore k = \frac{1155 \text{ gal/hr}}{1000 \text{ cu.ft}} = \frac{1.155 \text{ gal}}{\text{hr.ft}^3 \text{ cat.}}$$

For the new plant, with $v_0 = 5500 \text{ gal/hr}$, $X_F = .46$, the required catalyst volume is:

$$V = \frac{-v_0}{k} \ln(1-X_F) = \frac{-5500 \text{ gal/hr}}{1.155 \text{ gal/hr}} \ln(1-.46) = 2531 \text{ ft}^3 \text{ cat.}$$

This assumes that the same hydrodynamic conditions are present in the new reactor as in the old.

P4-15. Given $A \rightarrow B$ in a tubular reactor



$L_t = 40 \text{ ft}$ = length of reactor tubes

$D_t = .75 \text{ in}$ = tube diameter

$n_t = 50$ = number of tubes

$$\therefore V = \frac{n_t \pi D_t^2}{4} L_t =$$

$$(50)(.785)\left[\frac{.75 \text{ in}}{12 \text{ in/ft}}\right]^2 (40 \text{ ft}) = 6.13 \text{ ft}^3$$

$$F_{AO} = \frac{v_0}{(M_w)_A} = \frac{500 \text{ lb/hr}}{\frac{73 \text{ lb}}{\text{lbmole}}} = 6.86 \text{ lbmole/hr}$$

$$\left[\frac{v_0}{(M_w)_A} \right] = \frac{500 \text{ lb/hr}}{73 \frac{\text{lb}}{\text{lbmole}}}$$

$$V = F_{AO} \int_0^X \frac{dX}{-r_A}; -r_A = \frac{k C_{AO}(1-X)}{[1+KX]} = k C_{AO}(1-X)$$

$$\therefore V = F_{AO} \int_0^X \frac{dX}{-r_A} = F_{AO} \int_0^X \frac{dX}{k C_{AO}(1-X)} = \frac{F_{AO}}{k C_{AO}} \ln \frac{1}{1-X}$$

P4-15 (cont'd)

With $C_{AO} = \frac{P}{RT} = \frac{y_{AO}P}{RT}$, $V = \frac{F_{AO}RT}{k y_{AO}P} \ln \frac{1}{1-X}$ eqn. (a)

Assume Arrhenius equation applies to the rate constant

at $T_1 = 600^\circ R$ $k_1 = .00152$; $k_1 = A e^{-E/RT_1}$

at $T_2 = 760^\circ R$ $k_2 = .0740$; $k_2 = A e^{-E/RT_2}$

$\frac{k_2}{k_1} = e^{-E/R (\frac{1}{T_2} - \frac{1}{T_1})}$; $\therefore \ln \frac{k_2}{k_1} = -\frac{E}{R} (\frac{1}{T_2} - \frac{1}{T_1}) = \frac{E}{R} (\frac{T_2 - T_1}{T_1 T_2})$

$\therefore \frac{E}{R} = (\frac{T_1 T_2}{T_1 - T_2}) \ln \frac{k_2}{k_1} = \frac{(660)(760)^\circ R^2}{100^\circ R} \ln \frac{.0740}{.00152} = 19,500^\circ R$

$A = k_1 e^{+E/RT_1}$ $\therefore k = k_1 e^{-E/R (\frac{1}{T} - \frac{1}{T_1})}$

From Eqn. a,

$\frac{V}{T} = \frac{k_1 e^{-\frac{E}{R} (\frac{1}{T} - \frac{1}{T_1})}}{T} = \frac{F_{AO}^2}{V y_{AO} P} \ln \frac{1}{1-X_{AF}}$

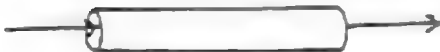
or $\frac{-19,500 [\frac{1}{T} - \frac{1}{660^\circ R}]}{T} = \frac{F_{AO} R}{k_1 V y_{AO} P} \ln \frac{1}{1-X_{AF}}$

$\frac{[6.86 \times 10^6 \text{ lbmol/s}]}{\text{hr}} \left[\frac{10.73 \text{ psia} \cdot \text{ft}^3}{1 \text{ lbmol} \cdot ^\circ R} \right] \ln 5$
 $\left[\frac{.00152}{\text{sec}} \right] = \frac{3600 \text{ sec}}{\text{hr}} [6.13 \text{ ft}^3] [114.7 \text{ psia}]$

$\frac{-19,500 [\frac{1}{T} - \frac{1}{660^\circ R}]}{T} = .0308^\circ R^{-1}$ Solving, $T = 738^\circ R = 278^\circ F$

P4-16.

Plug flow reactor $A \rightarrow B$



X_{Ad} = design conversion = 0.632

X_{Af} = actual conversion = $0.927 X_{Ad}$
 $= 0.586$

$\Theta_B = 0$; $y_{AO} = 1$; $\delta = 1 - 1 = 0$; $\epsilon = 0$

$-r_A = k C_{AO} (1-X)$

4-35

(2) Evaporation

Equations:

$$d(X)/d(z) = -ra \cdot w \cdot d / fao$$

$$k = 16e-5$$

$$w = 100$$

$$d = 0.25$$

$$cao = 0.01$$

$$vo = 2$$

$$Q = 1.11e-3$$

$$\rho = 55.5$$

$$fao = cao \cdot vo$$

$$fa = fao \cdot (1-X)$$

$$v = vo - Q \cdot w \cdot z / \rho$$

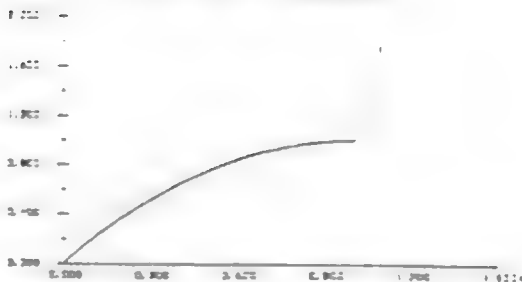
$$ca = fa / v$$

$$ra = -k \cdot ca$$

$$z_0 = 0, \quad z_f = 1100$$

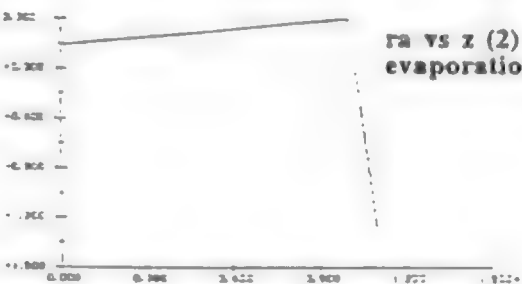
Key
X

x vs z (2) evaporation



Scale 10^4

Key
ra

ra vs z (2)
evaporation


(3) Evaporation and condensation

Equations:

$$d(X)/d(z) = -ra \cdot w \cdot d / fao$$

$$k = 16e-5$$

$$w = 100$$

$$d = 0.25$$

$$cao = 0.01$$

$$vo = 2$$

$$Q = (1.11e-3) - 0.5$$

$$\rho = 55.5$$

$$fao = cao \cdot vo$$

$$fa = fao \cdot (1-X)$$

$$v = vo - Q \cdot w \cdot z / \rho$$

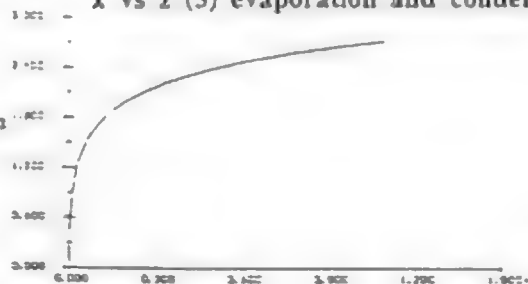
$$ca = fa / v$$

$$ra = -k \cdot ca$$

$$z_0 = 0, \quad z_f = 1100$$

Key
X

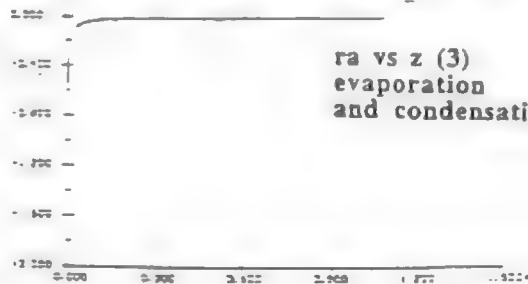
x vs z (3) evaporation and condensation



Scale 10^3

Scale 10^4

Key
ra

ra vs z (3)
evaporation
and condensation


d) Making the ratio Q/kC_{A0} a small positive number immediately puts the conversion close to 1. Conversely making that ratio any negative number makes the conversion go down very quickly.

e) No solution will be given.

P4-18.

a) Assume isothermal and $\varepsilon=0$

$$\text{therefore, } P = P_0 (1 - \alpha W)^3 \quad 1 = 10 (1 - 0.01 W)^3$$

$$W = 99g.$$

b)

$$\frac{dX}{dW} = \frac{-r_A}{F_{A0}}$$

$$\frac{P}{P_0} = (1 - W\alpha)^3$$

$$-r_A = kC_A$$

$$C_A = C_{A0} (1 - X) P/P_0$$

$$C_A = C_{A0} (1 - X) (1 - 0.01 W)^3$$

Integrate from $X=0$ to $X=.9$

$$\frac{dX}{dW} = \frac{kC_{A0}(1-X)}{F_{A0}} (1-0.01W)^3$$

$$W = 59.88g$$

First 5% conversion integrate from $X=0$ to $X=.05$

$$W = 1.31g$$

Last 5% conversion integrate from $X=.85$ to $X=.90$

$$W = 10.85g$$

4-37

P4-19 (cont'd)

b) Since turbulent flow

$$\alpha_2 = \alpha_1 (G_2/G_1)^2 (D_{p1}/D_{p2}) (A_{C1}/A_{C2})$$

$$= \alpha_1 (1/4)^2 (1/2) = \alpha_1 / 32$$

$$\alpha_2 = .938 / 32 = .029$$

$$a_2 = a_1 (F_{w1}/F_{w2}), \quad C_{w1} = C_0$$

$$a_2 = a_1 (1 / (1/4)) = 4a_1 = 2.78$$

By using trial and error in POLYMATH we get X=0.861

P4-20

PBR

$$\frac{dX}{dW} = \frac{kC_s}{F_{A0}} = \frac{kC_{A0} (1-X)}{F_{A0} (1+\epsilon X)},$$

$$\frac{dy}{dW} = \frac{-(1+\epsilon X)\alpha}{2y}$$

$$a = \frac{kC_{A0}}{F_{A0}}$$

Trial and error by POLYMATH gets us the following

Guess a, α , ϵ

at X = 0.064 y = .123

a = .000101, α = .000948, ϵ = 1

Equations:

$$d(x)/d(w) = a * (1-x) / (1+eps*x) * y$$

$$d(y)/d(w) = -(1+eps*x) * alp / (2*y)$$

$$alp = .000948$$

$$a = .000101$$

$$eps = 1$$

$$w_0 = 0, \quad w_f = 1000$$

Initial value

0

1

P4-20 cont'd

a) Mole balance:

$$W = \frac{F_{A0}X}{-r_A}$$

rate law:

$$-r_A = kC_A$$

Stoichiometry:

$$C_A = C_{A0} \frac{1-x}{1+\epsilon X}$$

Combine:

$$W = \frac{X(1+\epsilon X)}{a(1-X)}$$

$$X = 0.37$$

b)

$$\frac{dX}{dW} = \frac{a(1-X)}{1+\epsilon X} y$$

$$\frac{dy}{dW} = \frac{-(1+\epsilon X)\alpha}{2y}$$

We will make the approximation that ϵX will be neglected with respect to 1 and then use the above equations. k will increase as D_p will decrease as per Chapter 12 and that α increases as D_p decreases so that y decreases and there is a competition for the effect on $-r_A$. α also decreases as G decreases therefore y increases and rate also increases therefore higher conversion.

c) No solution will be given.

P4-21.

a) $P/P_0 = 1/20 = (1 - \alpha \cdot 1000 \text{ kg})^5 \quad \alpha = 9.975 \times 10^{-4} \text{ kg}^{-1}$

b) PBR

MB: $\frac{dX}{dW} = \frac{-r_A}{F_{A0}}$

Rate Law: $-r_A = k C_A$

$C_A = C_{A0}(1-X)$

Combine:

$$\int_0^{.141} \frac{dX}{1-X} = \left(\frac{k C_{A0}}{F_{A0}} \right) \int_0^W (1-W\alpha)^5 dW$$

$$.152 = \left(\frac{k C_{A0}}{F_{A0}} \right) \int_0^{1000} (1-8 \times 10^{-4} W)^5 dW$$

$$\frac{k C_{A0}}{F_{A0}} = 2 \times 10^{-4}$$

CSTR

MB: $W = \frac{F_{A0} X}{-r_A}$

Combine:

$$W = \frac{F_{A0}}{k C_{A0}} \frac{X}{(1-X)}$$

$$1000 = \frac{1}{2 \times 10^{-4}} \frac{X}{(1-X)}$$

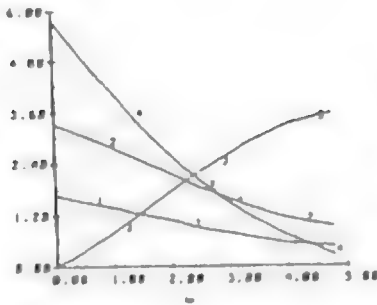
$$X = .18$$

- c) α is inversely proportional to cross sectional area and therefore the pipe diameter so increasing the diameter will decrease α . Since this is limited by internal diffusion, the specific reaction rate is inversely proportional to the particle diameter. So to increase the conversion it is wise to increase the pipe diameter and decrease the particle size.

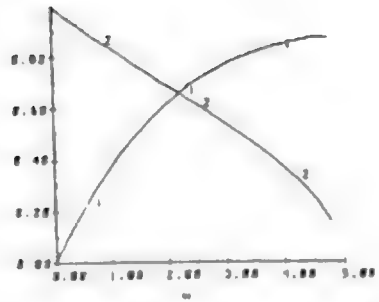
- d) Increase in cross sectional area decreases α . Increase in particle diameter decreases α . α could stay constant if cross sectional area is increased and particle diameter

P4-22 (cont'd)

KEY:
1 - p_a
2 - p_b
3 - p_c
4 - p_{ave}



KEY:
1 - α
2 - β



4-22 (c)

Case II $\alpha = 0.34$

$$C_A = C_{AO} \frac{(1-X)}{(1-0.66X)}$$

$$C_B = 2C_{AO} \frac{(1-X)}{(1-0.66X)}$$

$$C_C = \frac{C_{AO} X}{(1-0.66X)}$$

$$m_1 = m_2$$

$$G_1 \frac{\pi D_1^2}{4} = G_2 \frac{\pi D_2^2}{4}$$

$$G_2 = G_1 \left(\frac{D_1}{D_2} \right)^2$$

$$\text{Now } D_2 = 2 D_1$$

$$G_2 = \frac{1}{4} G_1$$

Slow Flow

$$\alpha = G$$

$$\alpha_2 = \frac{1}{4} \alpha_1$$

Rapid Flow

$$\alpha = G^2$$

$$\alpha_2 = \frac{1}{16} \alpha_1$$

Either way its a good idea

4-41

P4-22 (cont'd)

Case 1 $\alpha = 0$, $y = 1$

$$\frac{dX}{dW} = \frac{2k P_{AO}}{F_{AO}} \frac{(1-X)}{(1-66X)}$$

$$W = \frac{2k P_{AO}}{F_{AO}} \left[(1+\epsilon) \ln \frac{1}{1-X} - \epsilon X \right]$$

4-22 (a)

PFR without pressure drop

The equations:

$$d(x)/d(w) = -r_a / f_{a0}$$

$$y = 1$$

$$k = 1.74$$

$$P_{a0} = 0.333$$

$$r_a = -k P_{a0}^2 = -0.34 = (-0.666x) / (2+y)$$

$$f_{a0} = 13.33$$

$$\text{rate} = -r_a$$

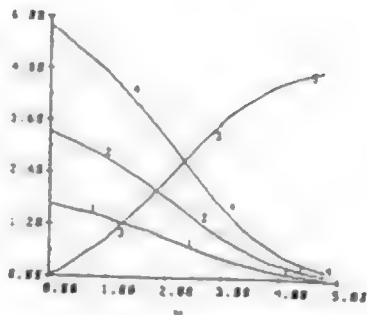
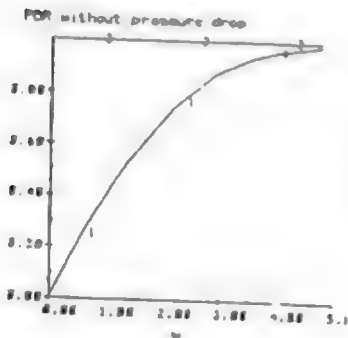
$$P_a = 0.333 = (1-x) / (1-0.666x)$$

$$P_b = 2 P_a$$

$$P_c = 0.333 + 5x = (-0.666x)$$

Initial values: $w_g = 0.0$, $x_g = 0.0$

Final value: $w_g = 4.0000$



4-22 (b)

PFR with pressure drop

The equations:

$$d(x)/d(w) = -r_a / f_{a0}$$

$$d(y)/d(w) = -0.34 = (-0.666x) / (2+y)$$

$$k = 1.74$$

$$P_{a0} = 0.333$$

$$r_a = -k P_{a0}^2 = -0.34 = (-0.666x) / (2+y)$$

$$f_{a0} = 13.33$$

$$\text{rate} = -r_a$$

$$P_a = 0.333 = (1-x) / (1-0.666x)$$

$$P_b = 2 P_a$$

$$P_c = 0.333 + 5x = (-0.666x)$$

Initial values: $w_g = 0.0$, $x_g = 0.0$, $y_g = 1.0000$

Final value: $w_g = 4.0000$

P4-23.

Solution:

Mole Balance

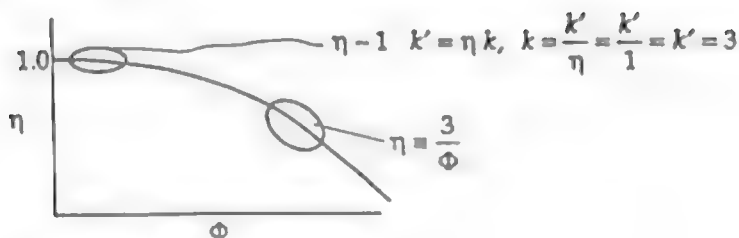
$$\frac{dX}{dW} = r'_A / F_{A0}$$

Rate Law

$$-r'_A = k' C_A^2$$

$$k' = k \eta = k \left[\frac{3}{\Phi^2} (\Phi \coth \Phi - 1) \right]$$

$$\Phi = c D_p$$

Large D_p , $c D_p \longrightarrow$ Increasing Particle Size

Then

$$\eta = \frac{3}{\Phi} = \frac{3}{c D_p}$$

$$\text{when } D_p = 2 \text{ mm, } K' = 0.06, \eta = \frac{K'}{k} = \frac{.06}{3} = 0.02$$

$$0.02 = \frac{3}{c(2)}$$

$$c = 75$$

$$\Phi = 75 D_p$$

Stoichiometry

$$\text{Gas, } \varepsilon = 0, C_A = C_{A0}(1-X)y$$

$$\frac{dy}{dW} = -\frac{\alpha}{2y}, \text{ where } \alpha = \alpha_1 \left(\frac{D_{p1}}{D_p} \right)$$

$$\alpha_1 = \frac{2\beta_c}{P_o(1-\phi)\rho_c A_c} = \frac{2(10^{-3} \text{ atm} \cdot \text{dm}^3)}{20 \text{ atm}(1-0.35)(2.65 \text{ kg/dm}^3)(0.82 \text{ dm}^2)} = 7.08 \times 10^{-5} \text{ kg}^{-1}$$

4-43

Combine

$$\frac{dX}{dW} = \left(\frac{k' C_A^2}{F_{A0}} \right) (1-X)^2 y^2 \quad \text{and} \quad \frac{dy}{dW} = -\frac{\alpha}{2y}$$

$$k' = k \left[\frac{1}{\Phi^2} (\Phi \coth \Phi - 1) \right] \quad \text{where } k = 3 \text{ and } \Phi = 75 D_p$$

$$\alpha = 7.08 \cdot 10^{-5} k_g \left(\frac{D_{r1}}{D_r} \right)$$

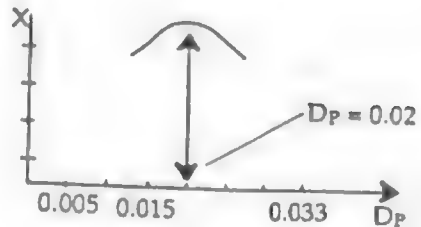
$$D_{r1} = 1, C_{A0} = 0.207, F_{A0} = 5$$

$$W = 0 \quad X = 0 \quad y = 1.0$$

$$W_f = 100$$

See POLYMATH program Vary D_p

D_p	α	y	η	k	X
1.0	$7.08 \cdot 10^{-5}$	0.996	.0039	0.12	0.092
0.1	0.0007	0.54	0.35	1.04	0.37
0.05	0.0014	0.93	0.59	1.76	.58
0.03	0.00236	0.87	0.77	2.3	0.64
0.025	.0028	0.85	0.82	2.5	0.65
0.015	.0035	0.73	0.92	2.8	0.64
0.01	.007	0.54	0.96	2.89	0.62
0.00725	.0098	0.15	0.98	2.4	0.56



c-23

Equations:

$$d(y)/d(w) = -\alpha/2/y$$

$$d(x)/d(w) = -r_a/f_{a0}$$

$$f_{a0} = 5$$

$$c_{a0} = 0.207$$

$$d_{p0} = 0.00725$$

$$k_1 = 3$$

$$\alpha_{p1} = 0.0000708$$

$$d_{p1} = 1$$

$$c_a = c_{a0} (1-x) \cdot y$$

$$\phi_1 = 75 \cdot d_p$$

$$\eta = 3/\phi_1 \cdot \left[1 - \left(\frac{\exp(\phi_1) - \exp(-\phi_1)}{\exp(\phi_1) + \exp(-\phi_1)} \right) \right]$$

$$\alpha = \alpha_{p1} \cdot d_{p1}/d_p$$

$$k = k_1 \cdot \eta$$

$$r_a = -k \cdot c_a^2$$

$$w_0 = 0, \quad w_f = 100$$

Plot

5/1/7

$$\frac{d(y)}{d(w)}$$

Initial value

1

0

$$C_a = C_{a0} (1-x) \cdot y, \quad \phi_1 = 75 \cdot d_p$$

$$\eta = \left[\frac{3}{\phi^2} (\phi \coth \phi - 1) \right]$$

1. Mole Balance : $\frac{dX}{dz} = \frac{-r_A A_c}{F_{A0}}$

2. Rate Law : $r_A = -k' C_A^2 \rho_c (1 - \varphi)$

where k' , ρ_c , and φ are unknown constants. They will be grouped into one unknown constant, k_o .

$$k_o = k' \rho_c (1 - \varphi)$$

3. Stoichiometry : $C_A = C_{A0} \frac{(1 - X)}{(1 + \epsilon X)}$

$$\epsilon = y_{A0} \delta = (1)(1 + \frac{1}{2} - 1) = \frac{1}{2}$$

4. Pressure Drop : $\frac{dy}{dz} = -\frac{\beta_o}{P_o y} (1 + \epsilon X)$

when neglecting the turbulent contribution to pressure drop, β_o is given by

$$\beta_o = G \left[\frac{150(1 - \varphi)^2 \mu}{\rho_o g_c D_p^2 \varphi^3} \right]$$

where all of the bracketed variables are unknown constants.

$$G = \frac{\dot{m}}{A_c}$$

The mass flow rate is also an unknown constant. Thus β_o can be written as a constant, B , over cross-sectional area.

$$\beta_o = \frac{B}{A_c} \quad \text{where} \quad B = \dot{m} \left[\frac{150(1 - \varphi)^2 \mu}{\rho_o g_c D_p^2 \varphi^3} \right]$$

Where B is a function of the mass flow rate, feed properties, and catalyst properties—all of which are constant for part (a). Note that all equations up to now apply to a tubular PBR and spherical PBR. To find B and k_o we must model the tubular PBR on POLYMATH by entering the above equations in addition to

$$A_c = \frac{\pi}{4} (20 \text{ dm})^2 = 314 \text{ dm}^2$$

B and k_o must be arbitrarily chosen at first. Then, depending on whether POLYMATH gives high or low values of y and X , one can converge on the true values of k_o and B . In order to do so efficiently, however, one must make use of the following trends: (Note that the following table is completely true only when $\epsilon > 0$.)

Case	POLYMATH y	POLYMATH X	Remedy	Effect on y	Effect on X
1	too HIGH	too HIGH	raise B	lowers y	lowers X
2	too HIGH	too LOW	raise k_0	lowers y	raises X
3	too LOW	too HIGH	lower k_0	raises y	lowers X
4	too LOW	too LOW	lower B	raises y	raises X

Once the correct values of B and k_0 are found, one can proceed with the standard spherical algorithm.

a) From POLYMATH:

$$B=843$$

$$b=0.21$$

$$x=67$$

$$P=yP_0=973 \cdot 1500=1459.5$$

Equations:

$$d(y)/d(z) = -\text{beta}/(p_0 \cdot y) \cdot (1 - \text{eps} \cdot x)$$

$$d(x)/d(z) = -r_a \cdot A_c / F_{a0}$$

$$p_0=1500$$

$$\text{eps}=0.5$$

$$F_{a0}=950$$

$$R=10$$

$$C_{a0}=0.4$$

$$k=0.21$$

$$B=843$$

$$A_c = 3.1416 \cdot (R^2 \cdot 2)$$

$$C_a = C_{a0} \cdot y \cdot (1-x) / (1 - \text{eps} \cdot x)$$

$$\text{beta} = B/A_c$$

$$r_a = k \cdot C_a^{0.2}$$

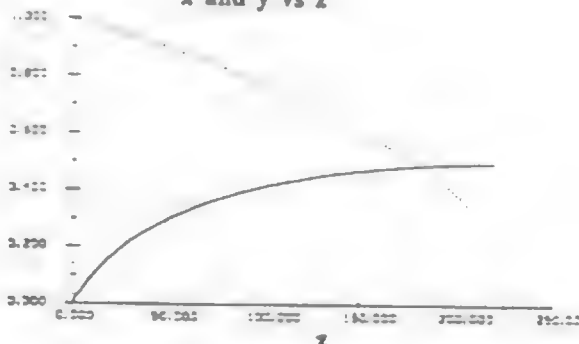
$$z_0 = 0, \quad z_f = 220$$

$$\text{eps} = 0.5$$

$$F_{a0} = 950 \frac{\text{Key}}{x}$$

$$--- y$$

x and y vs z



Equations:

$$d(y)/d(z) = -\beta / (p_0 \cdot y) \cdot (1 - \epsilon \cdot x)$$

$$d(x)/d(z) = -r_a \cdot A_c / F_{a0}$$

$$p_0 = 1500$$

$$\epsilon = 0.5$$

$$F_{a0} = 950$$

$$R = 26$$

$$C_{a0} = 0.4$$

$$k = 0.21$$

$$B = 843$$

$$L = 24$$

$$A_c = 3.1416 \cdot (R^2 - (z-L)^2)$$

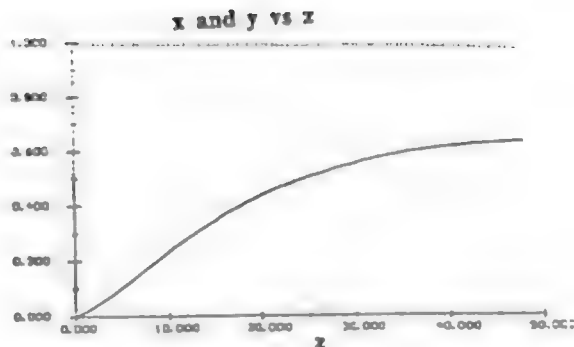
$$C_a = C_{a0} \cdot y \cdot (1-x) / (1-\epsilon \cdot x)$$

$$r_a = -k \cdot C_a^2$$

$$\beta = B / A_c$$

$$z_0 = 0, \quad z_f = 48$$

Key
— x
--- y



b) From POLYMATH:

maximum flowrate = 1750 mol/s

Equations:

$$d(y)/d(z) = -\beta / (p_0 \cdot y) \cdot (1 - \epsilon \cdot x)$$

$$d(x)/d(z) = -r_a \cdot A_c / F_{a0}$$

$$p_0 = 1500$$

$$\epsilon = 0.5$$

$$F_{a0} = 1750$$

$$R = 26$$

$$C_{a0} = 0.4$$

$$k = 0.21$$

$$B = 843$$

$$L = 24$$

$$A_c = 3.1416 \cdot (R^2 - (z-L)^2)$$

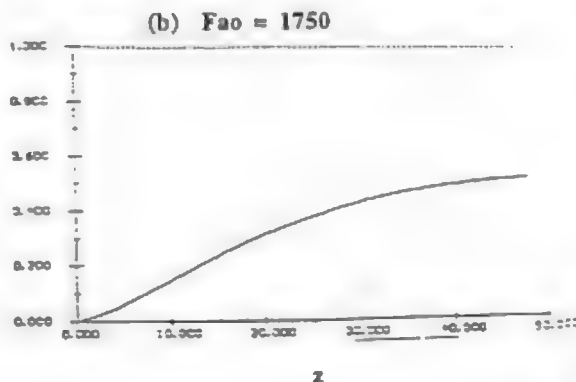
$$C_a = C_{a0} \cdot y \cdot (1-x) / (1-\epsilon \cdot x)$$

$$r_a = -k \cdot C_a^2$$

$$\beta = B / A_c$$

$$z_0 = 0, \quad z_f = 48$$

Key
— x
--- y



P4-24 (cont'd)

c) From POLYMATH

Minimum pressure=80 kPa

Equations:

$$d(y)/d(z) = -\text{beta}/(\text{po} \cdot y) \cdot (1 - \text{eps} \cdot x)$$

$$d(x)/d(z) = -\text{ra} \cdot \text{Ac}/\text{Fao}$$

$$\text{po} = 80$$

$$\text{eps} = 0.5$$

$$\text{Fao} = 950$$

$$\text{R} = 26$$

$$\text{Cao} = 0.4$$

$$\text{h} = 0.21$$

$$\text{B} = 44$$

$$\text{L} = 46$$

$$\text{Ac} = 3.1416 \cdot (\text{R}^2 - (\text{z} - \text{L})^2)$$

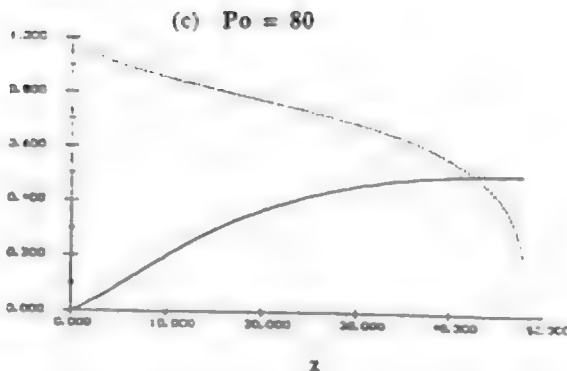
$$\text{Ca} = \text{Cao} \cdot y \cdot (1 - x) / (1 - \text{eps} \cdot x)$$

$$\text{ra} = \text{h} \cdot \text{Ca}^2$$

$$\text{beta} = \text{B}/\text{Ac}$$

$$z_0 = 0, \quad z_L = 46$$

Key
— x
--- y



d) From POLYMATH:

Equations:

$$d(y)/d(z) = -\text{beta}/(\text{po} \cdot y) \cdot (1 - \text{eps} \cdot x)$$

$$d(x)/d(z) = -\text{ra} \cdot \text{Ac}/\text{Fao}$$

$$\text{po} = 1500$$

$$\text{eps} = 0.5$$

$$\text{Fao} = 950$$

$$\text{R} = 26$$

$$\text{Cao} = 0.4$$

$$\text{h} = 0.21$$

$$\text{B} = 44$$

$$\text{L} = 46$$

$$\text{Ac} = 3.1416 \cdot (\text{R}^2 - (\text{z} - \text{L})^2)$$

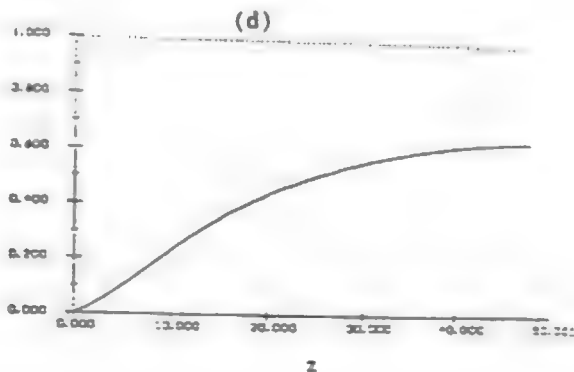
$$\text{Ca} = \text{Cao} \cdot y \cdot (1 - x) / (1 - \text{eps} \cdot x)$$

$$\text{ra} = \text{h} \cdot \text{Ca}^2$$

$$\text{beta} = \text{B}/\text{Ac}$$

$$z_0 = 0, \quad z_L = 46$$

Key
— x
--- y



4-25 No solution will be given

P4-26 (cont'd)

$$X_{Aeq} = \frac{-b - \sqrt{b^2 - 4ac}}{2a}$$

where

$$a = \left(1 - \frac{1}{K_e}\right)$$

$$b = \left(\frac{v_0 C_{B0} f}{N_{A0}} + 1\right) \quad c = \left(\frac{v_0 C_{B0} f}{N_{A0}}\right)$$

4-26 (a)

The equations:

$$d(\text{vol})/dt = 0.05$$

$$d(na)/dt = -r_{\text{vol}}$$

$$d(nb)/dt = 0.05 \times 0.93 - r_{\text{vol}}$$

$$d(nc)/dt = r_{\text{vol}}$$

$$d(nd)/dt = r_{\text{vol}}$$

$$r = 9 \times 10^{11} \times (-5) \times (na/\text{vol}) \times (nb/\text{vol}) - (1 \times nc/\text{vol}) \times (nd/\text{vol}) \times (1.08)$$

$$x_a = (1544 - na) / 1544$$

$$x_b = (0.05 \times 0.93 \times t - nb) / (0.05 \times 0.93 \times t - 1.38 \times (-10))$$

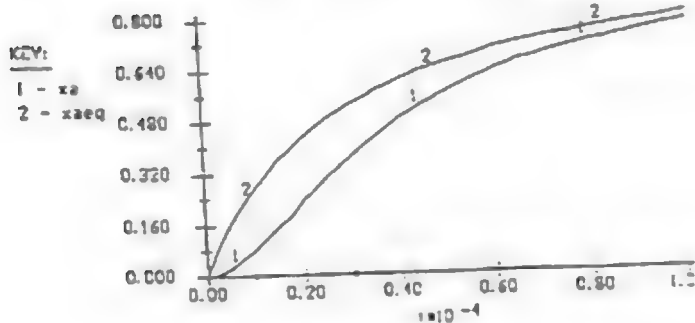
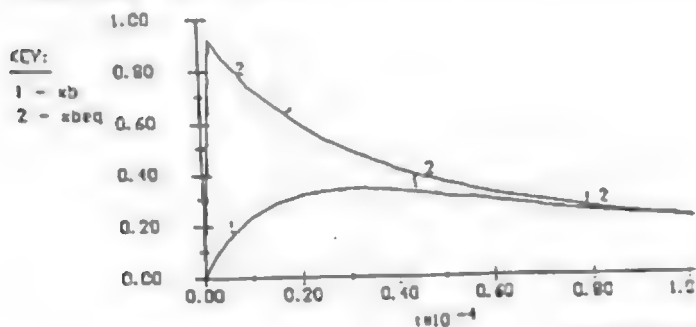
$$b = (-0.05 \times 0.93 \times t / 1544 + 1)$$

$$x_{aeq} = (-b - (b^2 - 4 \times 0.74) \times (-b - 1)) \times 0.5 \times (2 \times (1 - 1/1.08))$$

$$x_{beq} = (1544 / (0.05 \times 0.93 \times t + 1.38 \times (-3))) \times x_{aeq}$$

Initial values: $t_0 = 0.0$, $\text{vol}_0 = 200.00$, $n_{a0} = 1544.0$, $n_{b0} = 0.0$, $n_{c0} = 0.0$, $n_{d0} = 0.0$

Final values: $t_f = 0.100 \times 10^5$



4.49

The equations:

$$d(\text{vol})/dt = .05$$

$$d(\text{na})/dt = -r \cdot \text{vol}$$

$$d(\text{nb})/dt = .05 \times 0.93 - r \cdot \text{vol}$$

$$d(\text{nc})/dt = r \cdot \text{vol}$$

$$d(\text{nd})/dt = r \cdot \text{vol}$$

$$r = 9 \times 10^3 \times (-5) \times ((\text{na}/\text{vol}) \times (\text{nb}/\text{vol}) - ((\text{nc}/\text{vol}) \times (\text{nd}/\text{vol}))) / 1.08$$

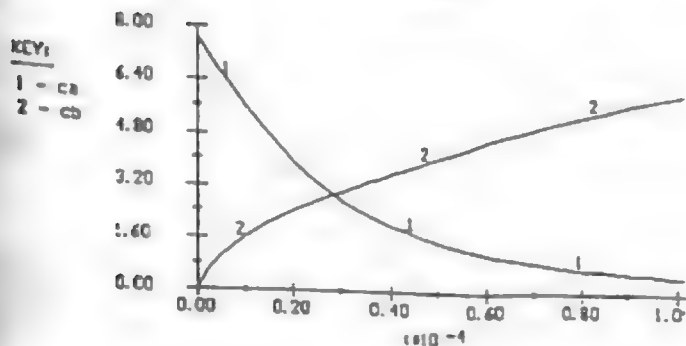
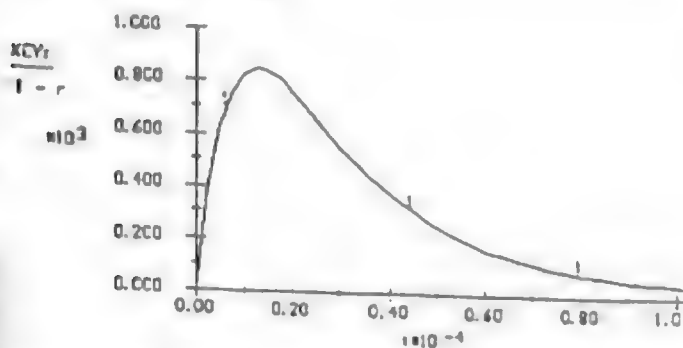
$$\text{xa} = (1544 - \text{na}) / 1544$$

$$\text{xb} = (.05 \times 0.93 \times 1 - \text{nb}) / (.05 \times 0.93 \times (1 + 1.2 \times (-10)))$$

$$\text{b} = (.05 \times 0.93 \times 1 / 1544 \times 1)$$

$$\text{ca} = \text{na} / \text{vol}$$

$$\text{cb} = \text{nb} / \text{vol}$$

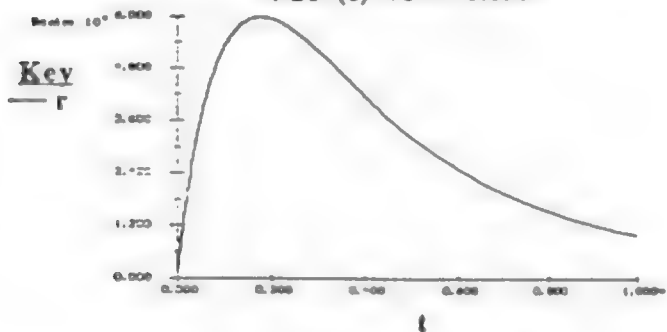
Initial values: $r_0 = 0.0$, $\text{vol}_0 = 200.00$, $\text{na}_0 = 1544.0$, $\text{nb}_0 = 0.0$, $\text{nc}_0 = 0.0$, $\text{nd}_0 = 0.0$ Final value: $t_f = 0.100 \times 10^5$ 

P4-26 (cont'd)

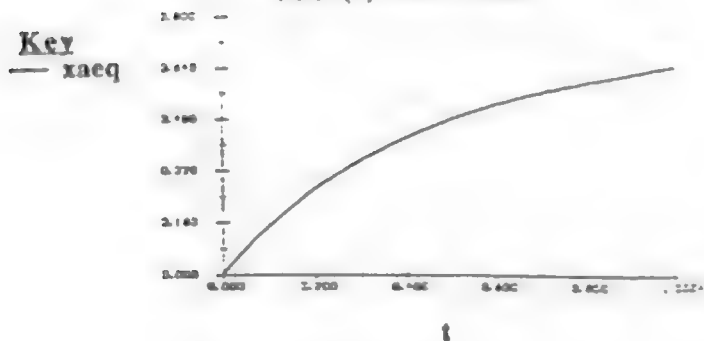
(c) Using the same POLYMATH equations, and changing values for V and v_o .

Change v_o from $0.050 \text{ dm}^3/\text{s}$ from $0.025 \text{ dm}^3/\text{s}$:

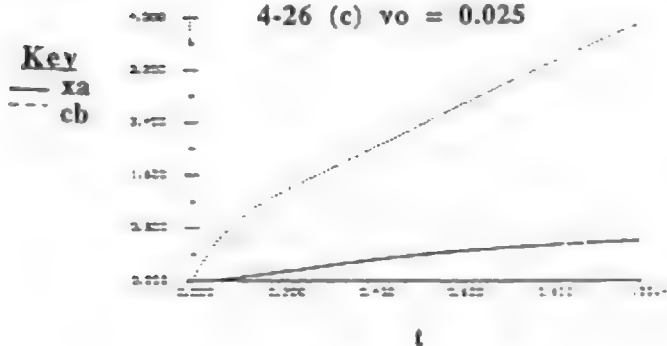
4-26 (c) $v_o = 0.025$



4-26 (c) $v_o = 0.025$



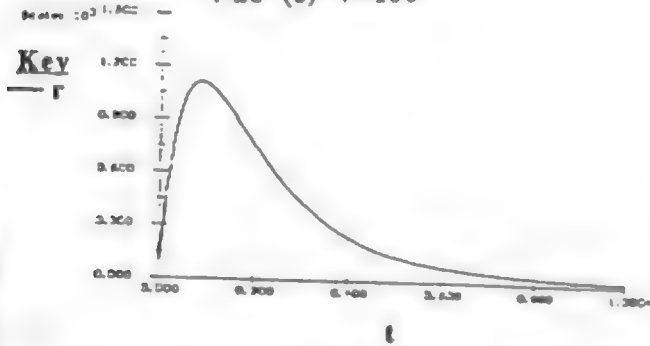
4-26 (c) $v_o = 0.025$



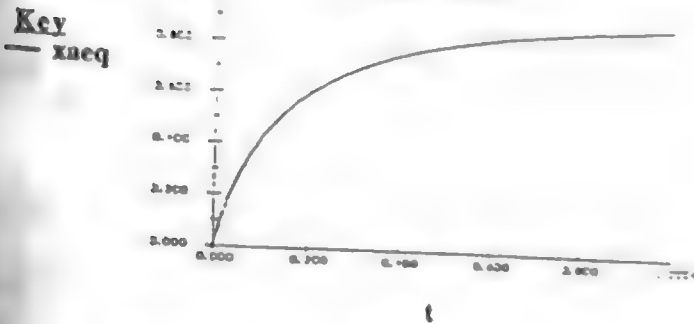
P4-26 (cont'd)

Change V from 200 dm^3 to 100 dm^3 :

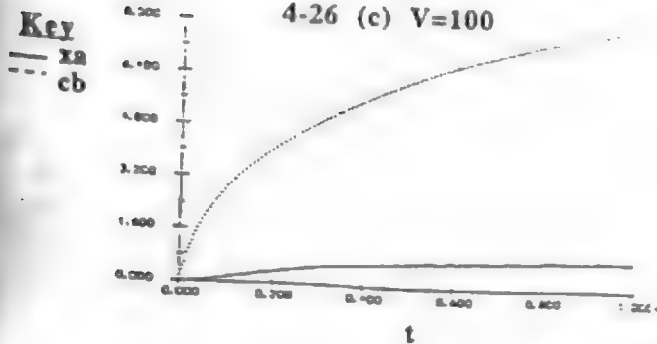
4-26 (c) $V=100$



4-26 (c) $V=100$



4-26 (c) $V=100$



P4-26 (cont'd)

- (d) Evaporation of D at a rate of 0.5 mol/s changes the mole balance for species D.

$$\frac{dN_D}{dt} = -0.5 + rV$$

Simulations show that N_D is always negative. Therefore, set

$$\frac{dN_D}{dt} = 0, \text{ where } N_D = 0 \text{ at } t = 0$$

See POLYMATH solution below.

4-26 (d)

The equations:

$$d(\text{vol})/dt = 0.05$$

$$d(na)/dt = -r \times \text{vol}$$

$$d(nb)/dt = 0.05 \times 10.93 - r \times \text{vol}$$

$$d(nc)/dt = r \times \text{vol}$$

$$d(nd)/dt = 0.0$$

$$r = 9 \times 10^4 \times (-5) \times ((na/\text{vol}) \times (nb/\text{vol}) - ((nc/\text{vol}) \times (nd/\text{vol}))) / 1.08$$

$$xa = (1544 - na) / 1544$$

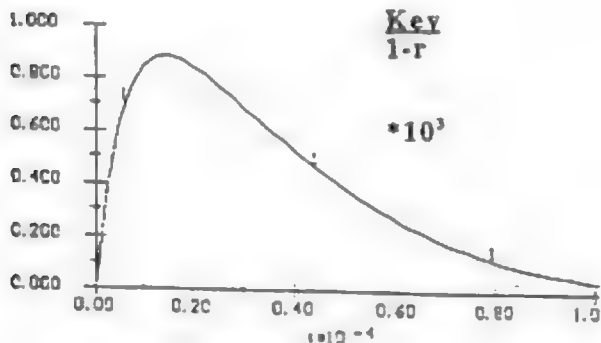
$$xb = (0.05 \times 10.93 \times t - nb) / (0.05 \times 10.93 \times (1 + 1. \times (-10)))$$

$$ca = na/\text{vol}$$

$$cb = nb/\text{vol}$$

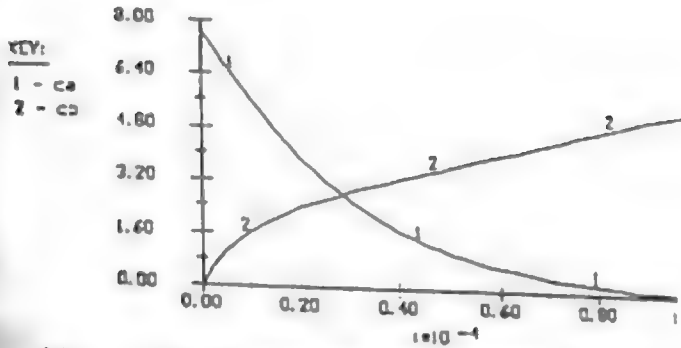
Initial values: $t_0 = 0.0$, $\text{vol}_0 = 200.00$, $na_0 = 1544.0$, $nb_0 = 0.0$, $nc_0 = 0.0$, $nd_0 = 0.0$

Final value: $t_f = 0.100 \times 10^5$

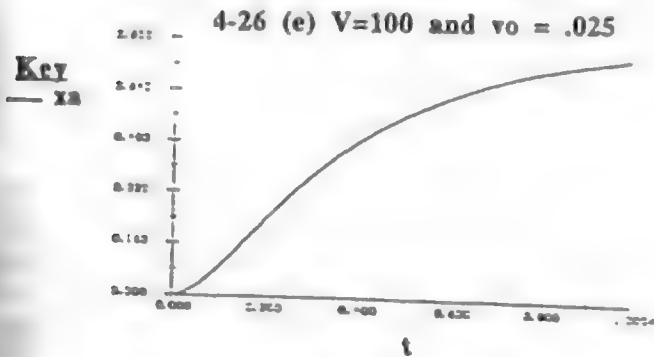


4-53

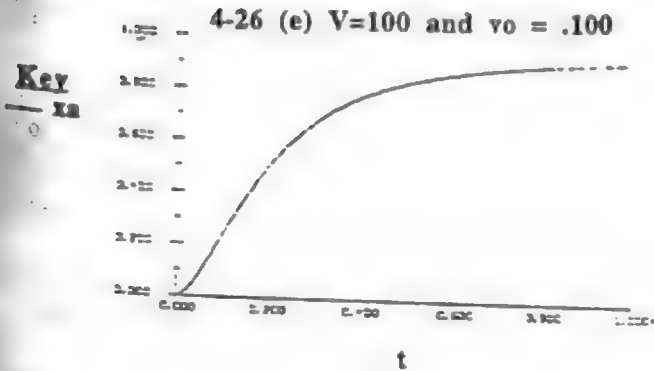
P4-26 (cont'd)



- (e) Using the same equations in POLYMATH and varying v_0 and V .
 $V = 100 \text{ dm}^3$ and $v_0 = 0.025 \text{ dm}^3/\text{s}$

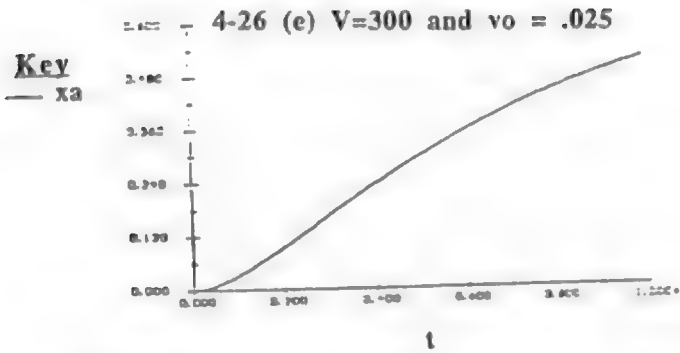


$V = 100 \text{ dm}^3$ and $v_0 = 0.100 \text{ dm}^3/\text{s}$

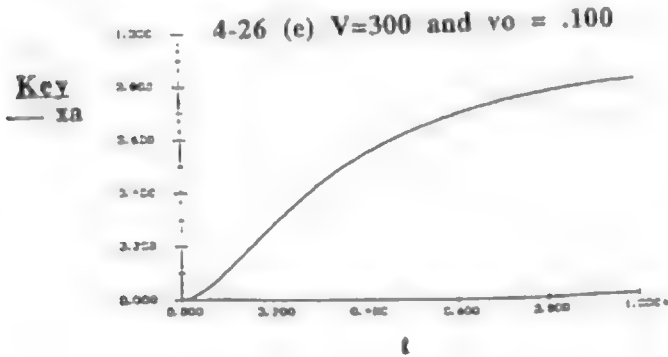


P4-26 (cont'd)

$V = 300 \text{ dm}^3$ and $v_o = 0.025 \text{ dm}^3/\text{s}$



$V = 300 \text{ dm}^3$ and $v_o = 0.100 \text{ dm}^3/\text{s}$



P4-27.



$$-r_A = k C_A C_B, k = 0.2 \text{ ft}^3/\text{lbmol min}$$

$$C_{A0} = 2 \text{ lbmol/ft}^3, C_{B0} = 0$$

$$V_0 = 100 \text{ ft}^3$$

$$v = 5 \text{ ft}^3/\text{min}, C'_{B0} = 0.5 \text{ lbmol/ft}^3$$

$$a) N_{A0} = C_{A0} V_0 = 2(\text{lbmol/ft}^3) 100(\text{ft}^3) = 200 \text{ lbmol}$$

$$V = V_0 + vt$$

$$N_c = N_{A0} X$$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0 + vt}$$

$$C_B = \frac{N_B}{V} = \frac{C'_{B0} vt}{V_0 + vt}$$

—Note that B is used at same rate as it is produced

$$-r_A = k C_A C_B = k \frac{N_{A0}(1-X) C'_{B0} vt}{(V_0 + vt)^2}$$

$$-r_A V = N_{A0} \frac{dX}{dt}$$

$$\frac{k N_{A0}(1-X) C'_{B0} vt}{V_0 + vt} = N_{A0} \frac{dX}{dt}$$

$$\frac{dX}{dt} = \frac{k C'_{B0} vt(1-X)}{V_0 + vt}$$

$$\int_0^X \frac{dX}{1-X} = \int_0^X \frac{k C'_{B0} v t}{V_0 + vt} dt$$

$$-\ln(1-X) = k C'_{B0} v \left[\frac{t}{v} - \frac{V_0}{v^2} \ln(V_0 + vt) \right]_0^{30}$$

$$-\ln(1-X) = k C'_{B0} \left[30 - \frac{V_0}{v} (\ln(V_0 + 30v) - \ln(V_0)) \right]$$

$$-\ln(1-X) = (0.2) \frac{\text{ft}^3}{\text{lbmol min}} (0.5) \frac{\text{lbmol}}{\text{ft}^3} \left[30 \text{ min} - \frac{100 \text{ ft}^3}{5 \text{ ft}^3/\text{min}} (\ln(100 + 30(5)) - \ln(100)) \right]$$

4.56

P4-27 (cont'd)

$$-\ln(1-X) = 0.1[30-20(0.916)] = 1.167$$

$$X = 0.689$$

$$N_c = N_{AO} X = (200) \text{ lbmol} (0.689) = 137.80 \text{ lbmol C}$$

$$b) -\ln(1-X) = k C'_{BO} \left[t - \frac{V_0}{v} \ln(V_0 + vt) \right] \Big|_0^t$$

$$-\ln(1-X) = (0.2)(0.5) \left[t - \frac{100}{5} (\ln(100+5t) - \ln(100)) \right]$$

$$\ln(1-X) = -0.1t + 2 \ln(100+5t) - 2\ln(100)$$

$$1-X = e^{-0.1t} (100+5t)^2 (100)^{-2}$$

$$X = 1 - \left(\frac{100+5t}{100} \right)^2 e^{-0.1t}$$

<u>t(min)</u>	<u>X</u>
0	0
5	0.052
10	0.172
15	0.317
20	0.459
25	0.584
30	0.689
35	0.772
40	0.835
45	0.883
50	0.917
55	0.943
60	0.960
10,000	1

$$c) C_A = \frac{N_A}{V} = \frac{C_{AO} v t - N_{BO} X}{V_0 + vt}$$

$$C_B = \frac{N_B}{V} = \frac{N_{BO}}{V_0 + vt}$$

-Note that B is used up at the same rate as it is produced.

$$N_c = N_{BO} X$$

$$N_{BO} = C_{BO} V_0 = (0.5) \text{ lbmol/ft}^3 (100) \text{ ft}^3 = 50 \text{ lbmol}$$

$$-r_A = k C_A C_B = \frac{k(C_{AO} v t - N_{BO} X) N_{BO}}{(V_0 + vt)^2}$$

P4-27 (cont'd)

$$-r_A V = N_{B0} \frac{dX}{dt}$$

$$N_{B0} \frac{k(C_{A0} - X) - N_{B0}X}{(V_0 + v_t)} = N_{B0} \frac{dX}{dt}$$

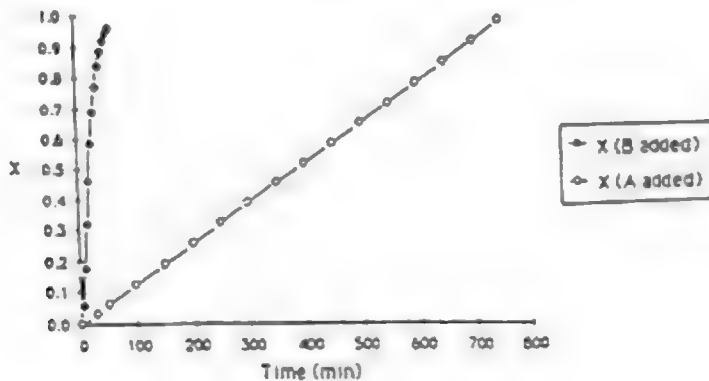
$$\frac{dX}{dt} = \frac{k(C_{A0} - X) - N_{B0}X}{V_0 + v_t}$$

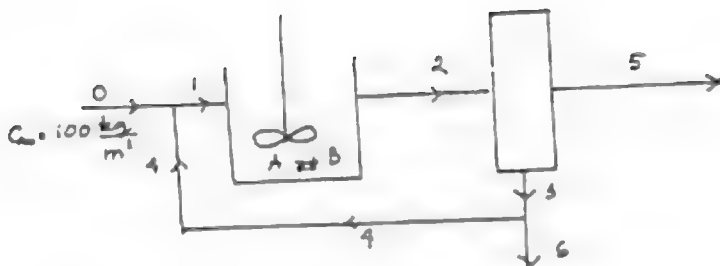
$$\frac{dX}{dt} = \frac{(0.2)((0.02)(5) - 50X)}{100+5t}$$

$$\frac{dX}{dt} = \frac{0.02t - 10X}{100+5t}$$

A modified version of the Runge-Kutta program yields:

t(min)	X	t(min)	X
0	0	650	0.853
30	0.0301	700	0.920
50	0.0597	750	0.987
100	0.122		
150	0.188		
200	0.254		
250	0.320		
300	0.387		
350	0.454		
400	0.520		
450	0.587		
500	0.653		
550	0.720		
600	0.787		





Note - A and B have the same molecular weight

$$F_{A2} = F_{A3}$$

$$F_{A4} = \gamma F_{A3}$$

$$F_{A1} = F_{A0} + \gamma F_{A3}$$

$$F_{A2} = F_{A1} (1-X) \text{ where } X \text{ is conversion defined with respect to } F_{A1}$$

$$F_{A5} = F_{B2} \text{ (by problem specification)}$$

$$F_{B1} = 0 \text{ (by problem specification)}$$

$$F_{A1} = F_{A0} - \gamma F_{A1} (1-X) \text{ have } F_{A1} = \frac{F_{A0}}{1-\gamma(1-X)} \quad (1)$$

Stoichiometric table

Inlet

Outlet

$$F_{A1}$$

$$F_{A1}(1-X)$$

$$F_{B1}=0$$

$$F_{B1} + F_{A1}X = F_{A1}X$$

Hence

$$F_{B2} = F_{A1}X = \frac{F_{A0}X}{1-\gamma(1-X)}$$

Also

$$v_1 = v_0 + v_4$$

$$v_2 = v_3 + v_5$$

$$v_1 = v_2 \quad (\text{no volume change})$$

$$C_{A1} = \frac{F_{A1}}{v_1} = 100$$

$$v_1 = \frac{F_{A1}}{C_{A1}} = \frac{F_{A1}}{100}$$

P4-29.

This problem was solved using POLYMATH. The equations used for parts a, b, and c are given below.

$$d(ca1)/d(t) = (((v_{oA}/v_0) \cdot ca_0 - ca1)/\tau) - k \cdot ca1^{**2}$$

$$d(ca2)/d(t) = ((ca1 - ca2)/\tau) - k \cdot ca2^{**2}$$

$$d(ca3)/d(t) = ((ca2 - ca3)/\tau) - k \cdot ca3^{**2}$$

$$\tau = 18$$

$$k = 0.025$$

$$ca_0 = 2$$

$$v_{oA} = 18$$

$$v_0 = 28$$

$$x = (v_{oA} \cdot ca_0 - v_0 \cdot ca3) / (v_{oA} \cdot ca_0)$$

$$t_0 = 0$$

$$ca1_0 = 0$$

$$ca2_0 = 0$$

$$ca3_0 = 0$$

$$t_f = 78$$

a) From POLYMATH, the steady state conversion of A is approximately 0.39.

b) 99% of the steady state concentration of A (the concentration of A leaving the 3rd reactor) is:

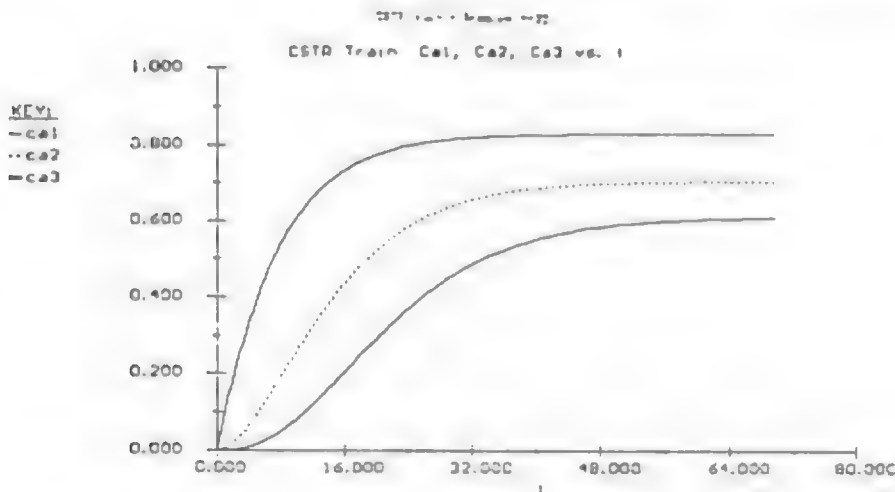
$$(0.99)(0.6110) = (0.605)$$

A concentration of 0.605 mol/dm³ of A corresponds to a time of approximately 64.0 minutes.

c) Below is a plot of the concentration of A exiting each reactor as a function of time.

P4-29 (cont'd)

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	70	0	70
ca1	0	0.828378	0	0.828378
ca2	0	0.703875	0	0.703875
ca3	0	0.608412	0	0.608412
voa	10	10	10	10
vo	20	20	20	20
cao	2	2	2	2
tau	10	10	10	10
k	0.025	0.025	0.025	0.025
x	1	1	0.391588	0.391588



d) From POLYMATH, we found the conversion to be 0.30

99% of the steady state concentration of A is

$$(0.99)(0.70) = (.693)$$

That corresponds to 48 minutes

Below is a plot of concentration of A exiting the three CSTRs as a function of time.

e) Varying any of the parameters effects the results rather dramatically. Increasing v_0 to 50 caused the conversion to go to .69 and decreasing it to 11 decreased the conversion to .12. Increasing V to 1000 dm³ increased the conversion to .87 while decreasing it to 20 dm³ caused the conversion to decrease to 0.068. Increasing k to .1 caused the conversion to increase to 0.67 while decreasing k to 0.001 caused the conversion to decrease to .054. A person can see that k and V have the most significant effects on the conversion in this case.

P4-29 (cont'd)

Equations:

$$d(ca1)/dt = ((voa/vo) * cao - ca1) / tau1 - k * ca1^{**2}$$

$$d(ca2)/dt = (ca1 - ca2) / tau2 - k * ca2^{**2}$$

$$d(ca3)/dt = (ca2 - ca3) / tau2 - k * ca3^{**2}$$

$$voa = 10$$

$$vo = 15$$

$$cao = 2$$

$$k = 0.025$$

$$tau1 = 13.3$$

$$tau2 = 10$$

$$x = (voa * cao - vo * ca3) / (voa * cao)$$

$$t_0 = 0, \quad t_f = 70$$

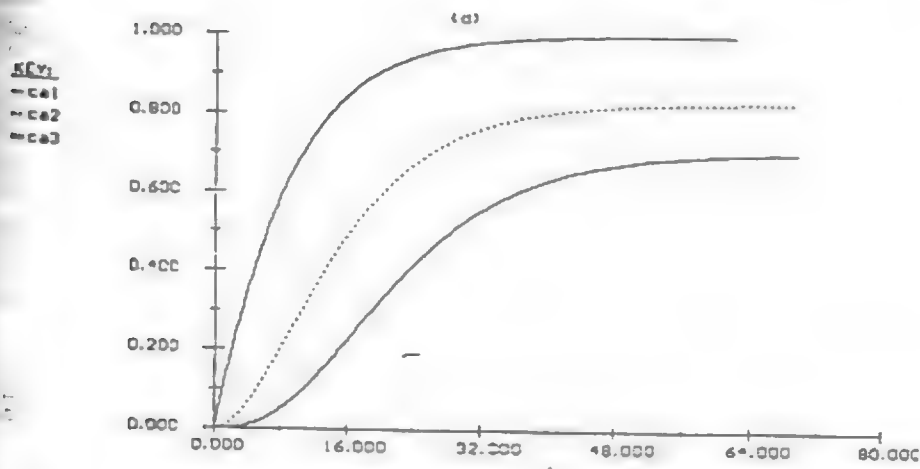
Initial value

0

0

0

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	70	0	70
ca1	0	1.00031	0	1.00031
ca2	0	0.82789	0	0.82789
ca3	0	0.701217	0	0.701217
voa	10	10	10	10
vo	15	15	15	15
cao	2	2	2	2
k	0.025	0.025	0.025	0.025
tau1	13.3	13.3	13.3	13.3
tau2	10	10	10	10
x	1	1	0.474088	0.474088



4-62

(a)

$$K_c = \frac{C_B}{C_A}$$

$$C_A = C_{A0}(1-X), \quad C_B = C_{A0}X$$

$$K_c = \frac{C_{A0}X}{C_{A0}(1-X)} = \frac{X}{1-X}$$

$$X_{eq} = \frac{K_c}{1+K_c} = \frac{0.5}{1+0.5} = 0.33$$

(b) For a conventional PFR:

$$F_{A0} \frac{dX}{dV} = -r_A$$

$$-r_A = k(C_A - C_B/K_c) = kC_{A0}((1-X) - X/K_c)$$

For the IMRCF:

$$\frac{dF_A}{dt} = r_A V_0$$

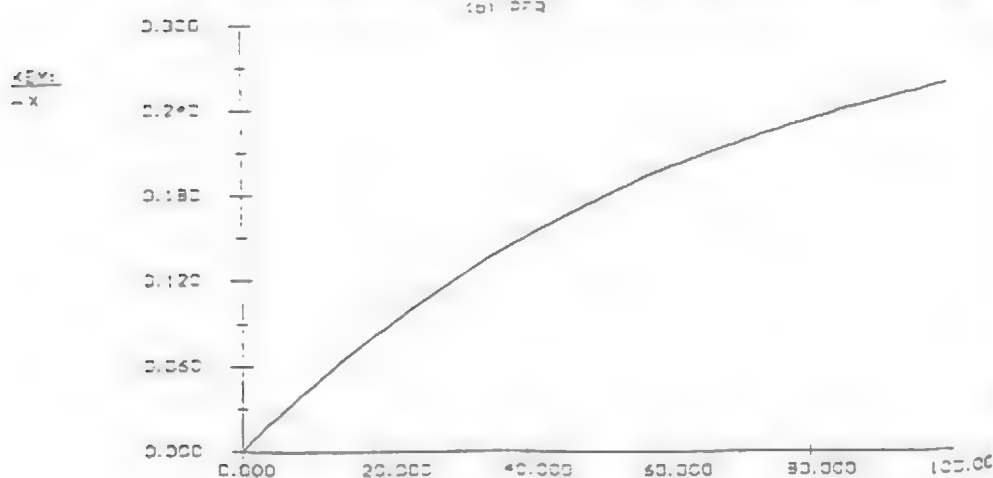
$$\frac{dF_B}{dt} = -r_A V_0 - V_0 k_c C_B$$

$$-r_A = k(C_A - C_B/K_c)$$

$$C_A = F_A/V, \quad C_B = F_B/V$$

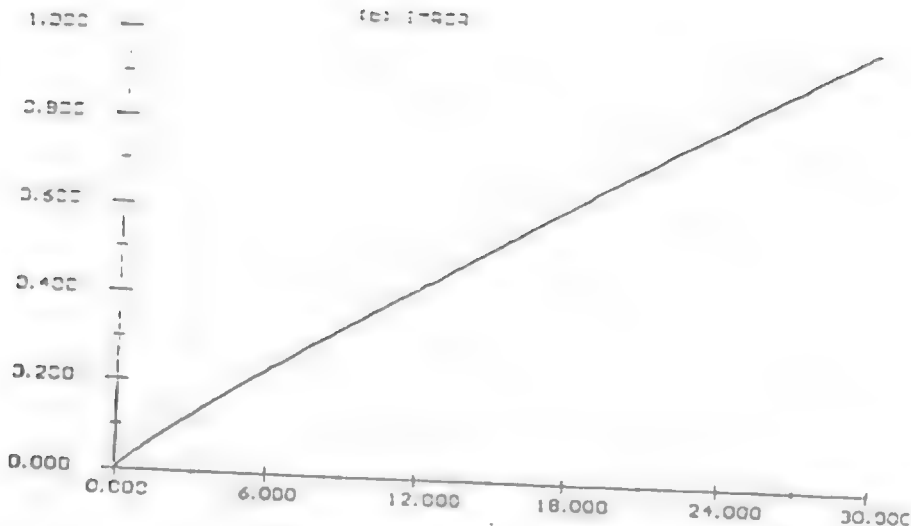
$$V = V_0 \frac{(F_A + F_B)}{F_{A0}}$$

Use these equations in POLYMATH to generate plots of the conversion profile.



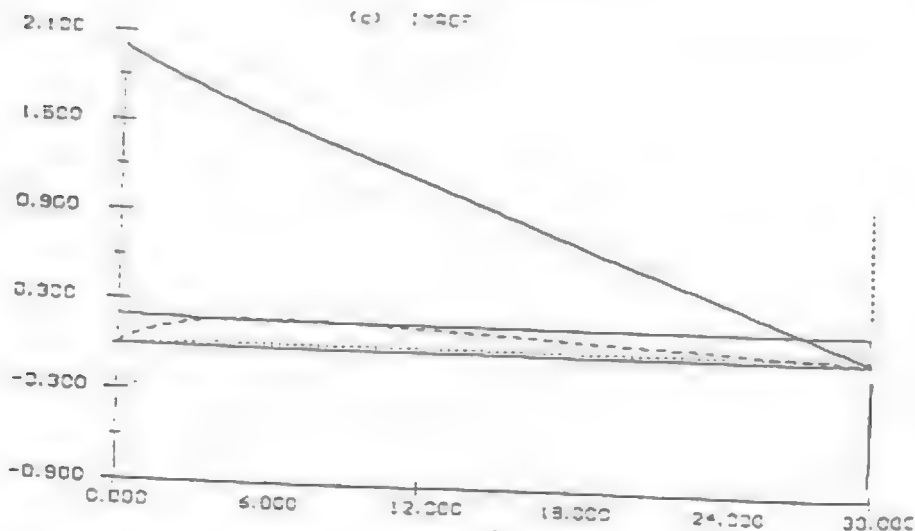
4-63

KEY:
-x



(c) Use the same equations for the IMRCF in POLYMATH to generate the desired plot.

KEY:
-ca
-cb
-fa
-fb



4-64

P4-30 (cont'd)

- (d) By varying one parameter at a time we can see the effect of each:

Increasing the specific reaction rate causes changes in conversion, concentration, and molar flow rate to occur more quickly.

Lowering the transport coefficient (k_t) causes an increase in both C_b and F_b , which causes a decrease in conversion.

By raising the equilibrium constant (K_p), we cause a decrease in the molar flow rate of A and an increase in conversion.

- (c) A significant increase in temperature for an exothermic reaction would drive the reaction in the reverse. This would cause a decrease in X and C, and an increase in the A.

A significant decrease in temperature for an exothermic reaction would cause increase in the rate of the forward reaction. This would drive up X and C_2 , while lowering C_1 .

An increase in temperature would drive an endothermic reaction forward, raising X and C_B , while lowering C_A .

A decrease in temperature would cause an increase in the reverse reaction for an endothermic reaction. This would raise C_A , and lower both X and C_B .

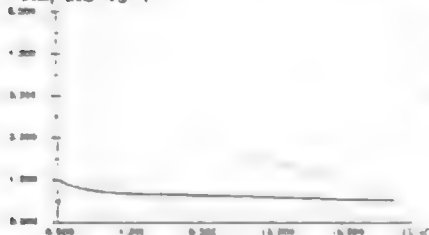
P4-31

- (a) Use the following POLYMATH program to generate the necessary graphs:

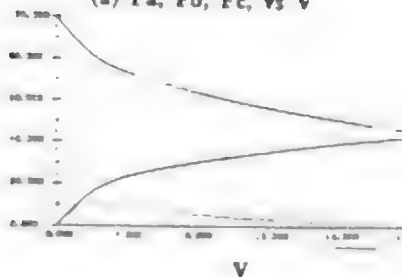
Equations	Variable	Initial value	Max. new value	Feasible value	Final value
$d(cb)/d(v) = -ca/Rb$	v	0	20	0	20
$d(fa)/d(v) = ca/Ra$	ca	0	1.3051	0	1.3051
$d(fc)/d(v) = -ra$	fa	100	100	45.3306	45.3306
$k=10$	rc	0	40.9875	0	40.9875
$kca=1$	k	10	10	10	10
$kcb=40$	kca	1	1	1	1
$vo=100$	kcb	40	40	40	40
$fao=100$	vo	100	100	100	100
$ke=.01$	fau	100	100	100	100
$fc=fa-fb-fc$	ke	0.01	0.01	0.01	0.01
$x=fc/(2*fao)$	fc	100	109.136	89.088	89.088
$vf=vo*fc/fao$	x	0	0.209318	0	0.209318
$ca=fa/vf$	vf	100	109.136	89.088	89.088
$cb=fb/vf$	ca	1	1	0.50883	0.50883
$cc=fc/vf$	cb	0	0.102812	0	0.0198659
$Ra=kca-fa/vf$	cc	0	0.471304	0	0.471304
$Rb=kcb-fb/vf$	Ra	1	1	0.53833	0.53833
$Rc=k* (ca-cb-cc)^2 ke$	Rb	0	0.794636	0	0.794636
$v_0 = 0, \quad v_f = 20$	Rc	-10	-1.375512	-10	-0.675512

4-65

Ra, Rb vs V



(a) Fa, Fb, Fc, vs V



(b) Conventional PFR

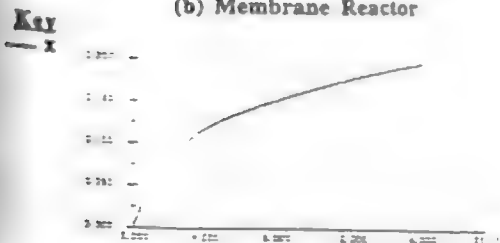
Mole Balance : $F_{A0} \frac{dX}{dV} = -r_A$

Rate Law : $-r_A = k(C_A - C_B C_C / K_C)$

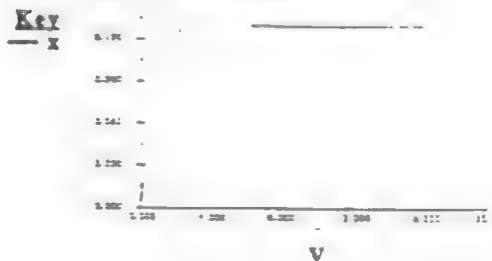
Stoichiometry : $C_A = C_{A0}(1-X)$, $C_B = C_{A0}X$, $C_C = 2C_{A0}X$

Use these equations and the program above in POLYMATH to generate curves for X vs. V.

(b) Membrane Reactor



(b) Conventional PFR





$$0.7 \text{ mol/l } \text{CH}_3\text{I} = C_{\text{BO}}$$

$$0.5 \text{ mol/l } \text{AgClO}_4 = C_{\text{AO}}$$

$$V_0 = 30 \text{ dm}^3$$

$$r_{\text{CH}_3\text{I}} = -k C_{\text{CH}_3\text{I}} C_{\text{AgClO}_4}^{3/2}$$

$$k = 0.00042 (\text{dm}^3/\text{mol})^{3/2} (\text{sec})^{-1} \quad T=298 \text{ K}$$

$$X = 0.98$$

$$\text{Let } A = \text{AgClO}_4, B = \text{CH}_3\text{I}$$

$$t = N_{\text{AO}} \int_0^X \frac{dX}{-r_A V}$$

$$V = V_0 \quad (\text{liquid phase})$$

$$t = \frac{C_{\text{AO}} V_0}{V_0} \int_0^X \frac{dX}{k C_B C_A^{3/2}}$$

$$t = \frac{C_{\text{AO}}}{k} \int_0^X \frac{dX}{C_{\text{AO}}^{7/5 - X} C_{\text{AO}}^{3/2} (1 - X)^{3/2}}$$

$$t = \frac{1}{k C_{\text{AO}}^{3/2}} \int_0^X \frac{dX}{(7/5 - X)(1 - X)^{3/2}}$$

Integration for $X = 0.98$, solved numerically

$$t = \frac{1}{0.00042 (0.5)^{3/2}} \quad (24.18)$$

$$t = 1.628 \times 10^5 \text{ sec} = 45.2 \text{ hr}$$

CDP4-B

(a)

$$\begin{aligned} \text{Mole Balance: } \frac{dN_A}{dt} &= F_{in} - F_A + r_A V \\ V \frac{dC_A}{dt} &= C_{A0} v_0 - C_A v_0 - k C_A V \\ \frac{dC_A}{dt} &= \frac{C_{A0} v_0}{V} - \frac{C_A (v_0 + V)}{V} \end{aligned}$$

Use POLYMATH to plot C_A vs. t

Equations:

$$d(C_A)/dt = (C_{A0} \cdot v_0 / V) - (C_A \cdot (k \cdot V + v_0) / V)$$

$$C_{A0} = 4.5$$

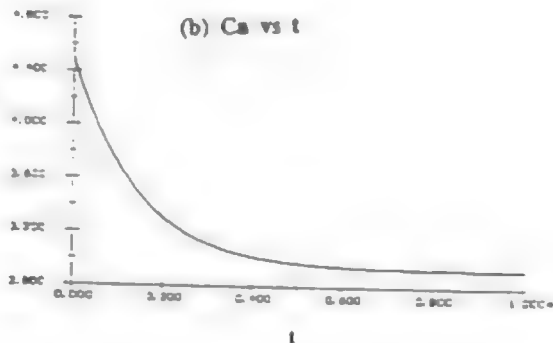
$$v_0 = 70000$$

$$V = 15000000$$

$$k = 0.0025$$

$$t_0 = 0, \quad t_f = 1000$$

Key
— C_A



For steady-state:

$$t = 4.6 \frac{\tau}{1 + k\tau} = 641 \text{ hrs}$$

$$C_A = \frac{C_{A0} v_0}{kV + v_0} = 2.930 \text{ mg/dm}^3$$

99% of this is 2.946 mg/dm^3 , which is below the standard of 3.0 mg/dm^3 .

(b)

$$\begin{aligned} \text{Mole Balance: } \frac{dN_A}{dt} &= F_{in} - F_A + r_A V \\ \frac{dN_A}{dt} &= C_{A0} v_0 - C_A v_0 - k C_A V \end{aligned}$$

Use POLYMATH to generate plot of C_A and N_A vs t .

CDP4-B (cont'd)

Equations:

$$d(na)/dt = cao \cdot vo - ca \cdot vout - k \cdot ca \cdot v$$

$$cao = 4.5$$

$$vo = 70000$$

$$vout = 50000$$

$$k = 0.0025$$

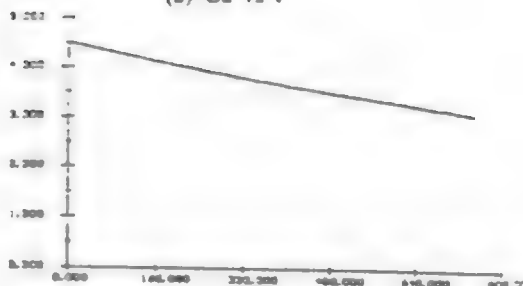
$$v = 20000 \cdot t$$

$$ca = na/v$$

$$t_0 = 1, \quad t_f = 750$$

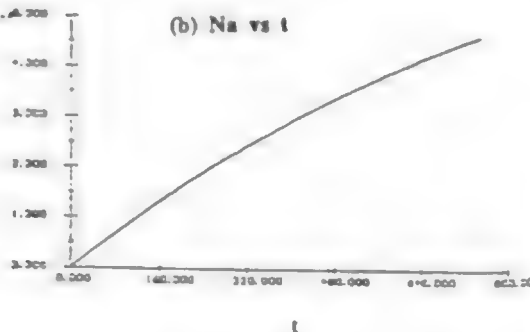
Key
— Ca

(b) Ca vs t



Key
— Na

(b) Na vs t



(c)

Use same equations as in part (a).

but change $C_{ao} = 4.5$ to $C_{ao} = 4.5 + 2.0 \cos\left(\frac{\pi}{8} t\right)$

Equations:

$$d(ca)/dt = (cao \cdot vo/v) - (ca \cdot (k \cdot v + vo)/v)$$

$$cao = 4.5 + 2 \cos(3.14159/8 t)$$

$$vo = 70000$$

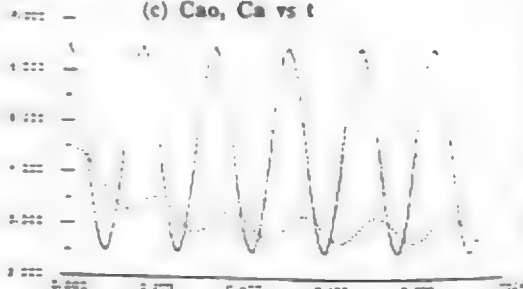
$$v = 15000000$$

$$k = 0.0025$$

$$t_0 = 0, \quad t_f = 1000$$

Key
— Cao
--- Ca

(c) Cao, Ca vs t



(d) Use the same equations in (a) except two values change:

$$V = 15000000 - 10000t$$

$$v_0 = 80000$$

The reason the graph looks so different from (a) is that pure water is evaporated, but water with atrazine is coming in.

4-b (a)

Equations:

$$d(ca)/dt = (cao \cdot v_0 / v) - (ca \cdot (k \cdot v + v_0) / v)$$

$$cao = 4.5$$

$$v_0 = 80000$$

$$v = 15000000 - 10000 \cdot t$$

$$k = 0.0025$$

$$t_0 = 0, \quad t_f = 1000$$

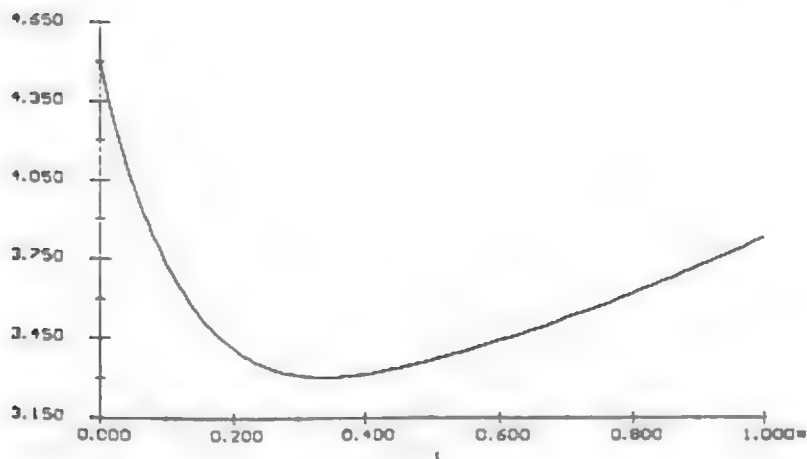
Initial value

4.5

4-b (d)

<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
t	0	1000	0	1000
ca	4.5	4.5	3.30411	3.8315
cao	4.5	4.5	4.5	4.5
v ₀	80000	80000	80000	80000
v	1.5e+07	1.5e+07	5e+06	5e+06
k	0.0025	0.0025	0.0025	0.0025

ca
- ca



4-70

CDP4-C

a) Find the number of moles of receptors:

$$1 \times 10^6 \frac{\text{cells}}{\text{mL}} \cdot 1 \times 10^5 \frac{\text{receptors}}{\text{cell}} \cdot \frac{1 \text{ mole receptors}}{6.022 \times 10^{23} \text{ receptors}} \cdot \frac{1000 \text{ mL}}{L} = 1.66 \times 10^{-10} \text{ M}$$

$$1.66 \times 10^{-10} \frac{\text{mol}}{L} \cdot .01 L = 1.66 \times 10^{-12} \text{ moles}$$

Design equation:

$$N_{A0} \frac{dX}{dt} = -r_A$$

Rate Law:

$$-r_A = k C_A C_B$$

Stoichiometry:

$$C_A = C_{A0}(1 - X)$$

$$C_B = C_{A0}(\theta_B - X)$$

Where:

Total number of moles:

$$1.66 \times 10^{-12} + 1 \times 10^{-9} = 1.002 \times 10^{-9}$$

hence:

$$y_A = \frac{1.66 \times 10^{-12}}{1.002 \times 10^{-9}} = 0.0017$$

$$y_B = \frac{1 \times 10^{-9}}{1.002 \times 10^{-9}} = 0.998$$

$$\theta_B = \frac{0.998}{0.0017} = 587$$

Combining and solving:

$$\frac{dX}{(1 - X)(\theta_B - X)} = \frac{k C_{A0}^2 dt}{N_{A0}}$$

$$\frac{1}{\theta_B - 1} \ln \frac{\theta_B - X}{\theta_B(1 - X)} = \frac{k C_{A0}^2 t}{N_{A0}}$$

$$t = 0.071 \text{ min}$$

b) Assume $C_B = C_{B0}$

Design Equation:

$$N_{A0} \frac{dX}{dt} = -r_A$$

Rate Law:

$$-r_A = k C_A C_B$$

Stoichiometry:

$$C_A = C_{A0}(1 - X)$$

$$C_B = C_{B0}$$

4-71

CDP4-C (cont'd)

Combine and solve:

$$\frac{dX}{1-X} = \frac{kC_{A0}C_{B0}dt}{N_{A0}}$$

$$\ln \frac{1}{1-X} = \frac{kC_{A0}C_{B0}t}{N_{A0}}$$

$$t=0.069 \text{ min}$$

A very good approximation.

c) Design Equation:

$$N_{A0} \frac{dX}{dt} = -r_A$$

Rate Law:

$$-r_A = k_f C_A C_B - k_r C_C$$

Stoichiometry:

$$C_A = C_{A0}(1-X)$$

$$C_B = C_{B0}$$

$$C_C = C_{A0}X$$

Combine and solve:

$$N_{A0} \frac{dX}{dt} = k_f C_{A0}(1-X)C_{B0} - k_r C_{A0}X$$

$$\frac{dX}{k_f C_{A0}C_{B0} - k_f C_{A0}C_{B0} - k_r C_{A0}X} = \frac{dt}{N_{A0}}$$

$$\int_0^X \frac{dX}{k_f C_{B0} - X(k_f C_{B0} + k_r)} = \int_0^t \frac{C_{A0} dt}{N_{A0}}$$

$$\frac{1}{k_f C_{B0} + k_r} \ln \frac{k_f C_{B0}}{k_f C_{B0} - X(k_f C_{B0} + k_r)} = \frac{5C_{A0}}{N_{A0}}$$

$$\frac{1}{.1+.1} \ln \frac{.1}{.1-X(.1+.1)} = 500$$

$$X = 0.5$$

$$-r_A = k_1 C_A C_B - k_2 C_A C_B^2$$

$$k_1 = 1.98 \text{ ft}^3/\text{lbmol}/\text{min}$$

$$k_2 = 9.2 \times 10^3 (\text{ft}^3/\text{lbmol})^2/\text{min}$$

$$V = 5 \text{ gal} = 0.67 \text{ ft}^3$$

$$C_{AO} = \frac{0.002 \text{ lbmol}}{0.67 \text{ ft}^3} = 2.98 \times 10^{-3} \text{ lbmol}/\text{ft}^3$$

$$C'_{AO} = \frac{0.34 \text{ lb}}{0.67 \text{ ft}^3} = 0.507 \text{ lb}/\text{ft}^3$$

$$C_{BO} = \frac{0.0018 \text{ lbmol}}{0.67 \text{ ft}^3} = 2.69 \times 10^{-3} \text{ lbmol}/\text{ft}^3$$

$$C'_{BO} = \frac{0.288 \text{ lb}}{0.67 \text{ ft}^3} = 0.430 \text{ lbmol}/\text{ft}^3$$

$$X = 0.65 \text{ based on A}$$

$$t = N_{AO} \int_0^X \frac{dX}{-r_A V}$$

$$V = V_0$$

(liquid phase)

$$t = \frac{C_{AO} - C}{V_0} \int_0^X \frac{dX}{(1+X)[k_1 C_A C_B + k_2 C_A C_B^2]}$$

$$t = C_{AO} \int_0^X \frac{dX}{(1+X)[k_1 C_{AO}^2 (1-X)(1-X/2) + k_2 C_{AO}^3 (1-X)(1-X/2)^2]}$$

$$t = \frac{C_{AO}}{C_{AO}^2} \int_0^X \frac{dX}{(1+X)(1-X)(1-X/2)[k_1 + k_2 C_{AO}(1-X/2)]}$$

$$t = \frac{1}{2.98 \times 10^{-3} \text{ ft}^3} \int_0^{0.65} \frac{dX}{(1-0.526X)(1-X)(1-X/2)[1.98 + (9.2 \times 10^3)(2.98 \times 10^{-3})(1-X/2)] \text{ ft}^3/\text{lbmole}/\text{min}}$$

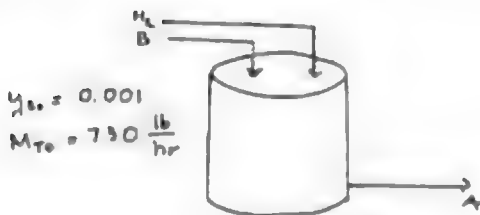
$$t = \frac{1}{2.98 \times 10^{-3}} \int_0^{0.65} \frac{dX}{(1-0.526X)(1-X)(1-X/2)(29.40-13.71X)}$$

Numerical integration yields

$$t = \frac{5.56 \times 10^{-2}}{2.98 \times 10^{-3}} \text{ min} = 18.7 \text{ min}$$

CDP4-E

Given: CSTR with reaction: $2 + B_2 \rightarrow A$



Finally

$$F_{AF} = F_{B_2}$$

$$F_{BF} = C_{BF} (etc)$$

$$Y_{BF} = 10^{-5}$$

$$V = 50 \text{ gal. liquid}$$

$$T = 100^\circ\text{C} = 373^\circ\text{K} = 672^\circ\text{R}$$

$$P = 500 \text{ psig}$$

$$-r_B = k C_{B_2} C_D$$

Liquid feed is a mixture of A and B. $\therefore y_{AO} = 1 - y_{BO} = .999$

Because of the low concentration of B in the feed, such properties as, SG, the specific gravity, MW, the molecular weight, and the solubility of B_2 are essentially that of component A. Assume that any B_2 depleted via reaction is instantaneously replaced via absorption of B_2 gas over the liquid reacting mixture. Then at 500 psig,

$$C_{B_2, f} = \left(\frac{5.0}{1} \right) \times \left(\frac{1 \text{ mole}}{28} \right) \times \left(\frac{1 \text{ lbmole}}{454 \text{ gmole}} \right) \times \left(\frac{3.785 \text{ l}}{\text{gal}} \right) = \frac{0.0208 \text{ lbmole}}{\text{gal}}$$

$$F_{AO} = F_{Af} \text{ because } y_B \ll 1, F_{Af} = \frac{\dot{V}_t}{(M_{WA})} = \frac{730 \text{ lb/hr}}{\frac{126 \text{ lb}}{\text{lbmole}}} = 3.72 \text{ lbmole/hr}$$

Assume that there is no volume change accompanying absorption of B_2 . Then

$$\therefore v_o = \frac{\dot{V}_t}{SG \rho_{H_2O}} = v = \text{constant, or}$$

$$v = \left(\frac{730 \text{ lb/hr.}}{1} \right) \times \left(\frac{1 \text{ lb} \times H_2O}{.980 \text{ lbA}} \right) = \left(\frac{1 \text{ ft}^3}{62.4 \text{ lb}} \right) \times \left(\frac{7.48 \text{ gal}}{\text{ft}^3} \right) = 69.3 \text{ gal/hr.}$$

4-74

CDP4-E (cont'd)

$$\text{X}_{B0} \frac{F_{T0}}{V_0}$$

$$C_{B0} = \frac{F_{B0}}{V_0} = \frac{F_{B0} F_{T0}}{V_0} = \frac{(10^{-3})(3.72) \text{ lbmole/hr}}{(89.3) \text{ gal/hr}} = 4.17 \times 10^{-5} \text{ lbmole/gal}$$

Using equation for a CSTR

$$V = \frac{F_{B0} X}{-r_B}$$

$$\tau = \frac{F_{B0} X}{V C_{B0} (1-X) C_{H_{2,f}}} = \frac{V_0 X}{V (1-X) C_{H_{2,f}}}$$

$$\tau = \frac{(89.3 \text{ gal/hr})(0.99)}{50 \text{ gal} \left(\frac{0.0208 \text{ lbmol}}{\text{gal}} \right) (0.01)}$$

$$\tau = 8.49 \times 10^3 \text{ gal/(lbmole-hr)}$$

With reactor at 300 psig, Henry's law is: $C_{H_2} \propto P$

$$\therefore C_{H_2} (300 \text{ psig}) = C_{H_2} (500 \text{ psig}) = \left(\frac{300+14.7}{500+14.7} \right) = (0.0208) \left(\frac{314.7}{514.7} \right) \frac{\text{lbmole}}{\text{gal}}$$

$$C_{H_2} = 0.0127 \text{ lbmole/gal}$$

Let conversion be X_2 when pressure = 300 psig

$$V = \frac{F_{B0} X_2}{C_{B0} (1-X_2) C_{H_{2,300}}} = \frac{V_0 X_2}{\tau (1-X_2) C_{H_{2,300}}}$$

$$\frac{X_2}{1-X_2} = \frac{(50 \text{ gal})(8.49 \times 10^3 \text{ gal/(lbmole-hr)})(0.0127 \text{ lbmol/gal})}{89.3 \text{ gal/hr}}$$

$$F_{H_{2,F}} = C_{H_{2,F}} V_0 = \left(\frac{0.0127 \text{ lbmole}}{\text{gal}} \right) (59.3 \text{ gal/hr}) = 1.134 \text{ lbmole/hr}$$

$$Y_{BF} = \frac{F_{B0} (1-X_2)}{F_{H_{2,F}} + F_{T0}} = \frac{(3.72 \times 10^{-3}) (1-0.984)}{1-1.134+3.72} = 1.23 \times 10^{-5}$$

a) Stoichiometric table - Basis: 1 mole of A fed

Species	In	Change	Out
A	1	-X	1-X
B	5/2	-2X	5/2-2X
D	0	+2X	2X
I	3/2	0	3/2
	5	-X	5-X

$$v = \frac{F_T}{F_{T_0}} v_0 = \frac{F_{A0} (5-X)}{5 F_{A0}} = (1-0.2X) v_0$$

$$b) C_A = \frac{F_A}{v} = \frac{F_{A0} (1-X)}{v_0 (1-0.2X)} = C_{A0} \frac{(1-X)}{(1-0.2X)}$$

$$C_B = \frac{F_B}{v} = \frac{F_{A0} (5/2-2X)}{v_0 (1-0.2X)} = C_{A0} \frac{(5/2-2X)}{(1-0.2X)}$$

$$C_D = \frac{F_D}{v} = \frac{F_{A0} (2X)}{v_0 (1-0.2X)} = C_{A0} \frac{(2X)}{(1-0.2X)}$$

$$c) C_{A0} = \frac{F_{A0}}{v_0} = \frac{y_{A0} F_{T_0}}{v_0} = \frac{y_{A0} P_{T_0}}{RT_0} = \frac{(0.2)(5 \text{ atm})}{(0.082) \text{ dm}^3 \text{ atm/mol K} (55+273) \text{ K}}$$

$$C_{A0} = 0.037 \text{ mol/dm}^3$$

$$d) -r_A = 2.5 C_A^{1/2} C_B = 2.5 C_{A0}^{3/2} \frac{(1-X)^{1/2} (5/2-2X)}{(1-0.2X)^{3/2}}$$

PFR

$$v = F_{A0} \int_0^X \frac{dX}{-r_A}$$

$$v = C_{A0} v_0 \int_0^X \frac{dX (1-0.2X)^{3/2}}{2.5 C_{A0}^{3/2} (1-X)^{1/2} (5/2-2X)}$$

$$v = \frac{C_{A0} v_0}{2.5 C_{A0}^{3/2}} \int_0^X \frac{(1-0.2X)^{3/2}}{(1-X)^{1/2} (5/2-2X)} dX$$

$$V = \frac{50 \text{ dm}^3/\text{min}}{(2.5)(0.037)^{1/2} (1/\text{min})} \int_0^{0.70} \frac{(1-0.2X)^{3/2}}{(1-X)^{1/2} (5/2-2X)} dX$$

$$V = 103.98 \int_0^{0.70} \frac{(1-0.2X)^{3/2}}{(1-X)^{1/2} (5/2-2X)} dX \text{ dm}^3$$

Numerical integration yields

$$V = 103.98 (0.483) \text{ dm}^3$$

$$V = 50.21 \text{ dm}^3$$

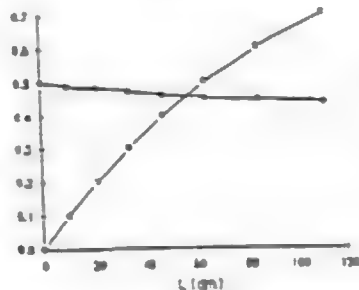
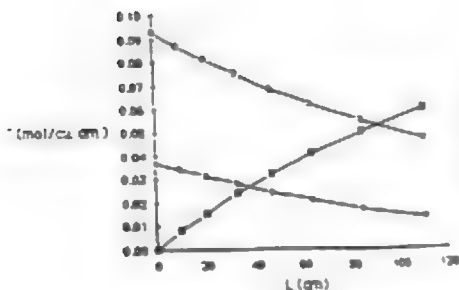
- a) Have C_A , C_B , C_D and v as functions of X , so only need an equation for X as a function of reactor length.

$$V = \pi r^2 L = \pi (0.76/2)^2 L = 0.454 L$$

$$\Rightarrow L = \frac{V}{0.454} = \frac{103.98}{0.454} \int_0^X \frac{(1-0.2X)^{3/2}}{(1-X)^{1/2} (5/2-2X)} dX$$

So if we take X from 0 to 0.70 in 0.10 intervals, we can get values of the other unknowns.

X	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
$C_A (\text{mol/dm}^3)$	0.037	0.034	0.031	0.028	0.024	0.021	0.017	0.013
$C_B (\text{mol/dm}^3)$	0.093	0.087	0.081	0.075	0.068	0.062	0.055	0.047
$C_D (\text{mol/dm}^3)$	0	0.008	0.015	0.024	0.032	0.041	0.050	0.060
$v (\text{dm}^3/\text{min})$	50	49	48	47	46	45	44	43
$V (\text{dm}^3)$	0	4.57	9.25	14.87	21.32	28.91	38.26	50.21
$L (\text{dm})$	0	9.62	20.38	32.75	46.93	63.67	84.28	110.59



b) CSTR

$$V = \frac{F_{AO}(X-X_0)}{-r_A} \quad \text{from } X=0.70 \text{ to } 0.85$$

$$V = \frac{C_{AO} v_0 (X-X_0)(1-0.2X)^{3/2} \text{ mol/min}}{2.5 C_{AO}^{3/2} (1-X)^{1/2} (5/2-2X) \text{ mol/dm}^3/\text{min}}$$

$$V = \frac{(50)(0.85-0.70)(1-0.2(0.85))^{3/2}}{2.5 (0.037)^{1/2} (1-0.85)^{1/2} (5/2-2(0.85))}$$

$$V = 38.06 \text{ dm}^3$$

$$b) -r_A = F_{AO} \frac{dX}{dV} = 2.5 C_A^{1/2} C_p$$

$$C_A = C_{AO} \frac{(1-X)}{(1-0.2X)} \frac{P}{P_0}; \quad C_B = C_{AO} \frac{(2.5-2X)}{(1-0.2X)} \frac{P}{P_0} \quad \text{where } \frac{P}{P_0} = (1-\alpha W)^{1/2}$$

$$-r_A = 2.5 C_{AO}^{3/2} \frac{(1-X)^{1/2} (2.5-2X)}{(1-0.2X)^{3/2}} (1-\alpha W)^{3/4} = F_{AO} \frac{dX}{dV}$$

$$\alpha = \frac{2\beta_0}{A_c(1-\delta)\rho_c P_0} \quad \beta_0 = \frac{G(1-\delta)}{\rho_0 g_c D_T \delta^3} \left[\frac{150(1-\delta)\mu}{D_p} + 1.75G \right]$$

$$A_c = \frac{\pi}{4} d^2 = \frac{\pi}{4} \left(\frac{1}{12}\right)^2 \text{ ft}^2 = 5.454 \times 10^{-3} \text{ ft}^2$$

$$\delta = 0.45$$

$$\rho_0 = 2 \text{ g/cm}^3 = 124.74 \frac{\text{lbm}}{\text{ft}^3}$$

$$P_0 = 5 \text{ atm}$$

$$\alpha = \frac{1}{A_c} \frac{[(0.037 \frac{\text{mol A}}{\text{dm}^3})(\frac{100 \text{ g A}}{\text{mol A}}) - (0.093 \frac{\text{mol B}}{\text{dm}^3})(\frac{50 \text{ g B}}{\text{mol B}})](50 \frac{\text{dm}^3}{\text{min}})}{5.454 \times 10^{-3} \text{ ft}^2}$$

$$\alpha = 7.653 \times 10^4 \frac{\text{ft}^2 \cdot \text{min}}{\text{ft}^2 \cdot \text{min}} = 168.61 \frac{\text{lbm}}{\text{ft}^2 \cdot \text{min}} = 10,117 \frac{\text{lbm}}{\text{ft}^2 \cdot \text{hr}}$$

$$\rho_0 = 0.4 \frac{\text{lbm}}{\text{ft}^3}$$

CDP4-F (cont'd)

$$s_c = 4.17 \times 10^8 \frac{\text{lbm ft}}{\text{lb f hr}^2}$$

$$D_p = 0.5 \text{ mm} = 5 \times 10^{-2} \text{ cm} = 1.64 \times 10^{-3} \text{ ft}$$

$$\mu = 0.0673 \frac{\text{lbm}}{\text{ft} \cdot \text{hr}}$$

$$\beta_o = \frac{(168.61 \frac{\text{lbm}}{\text{ft}^2 \cdot \text{min}})(0.55)(60 \frac{\text{min}}{\text{hr}})}{(0.4 \frac{\text{lbm}}{\text{ft}^3})(4.17 \times 10^8 \frac{\text{lbm ft}}{\text{lb f hr}^2})(1.64 \times 10^{-3} \text{ ft})(0.45)^3} \\ + \frac{(150)(0.55)(0.0673) \frac{\text{lbm}}{\text{ft} \cdot \text{hr}}}{1.64 \times 10^{-3} \text{ ft}} + (1.75)(10.117 \frac{\text{lbm}}{\text{ft}^2 \cdot \text{hr}})$$

$$\beta_o = (4708 \frac{\text{lb f}}{\text{ft}^3})(\frac{1 \text{ ft}^2}{144 \text{ in}^2})(\frac{1 \text{ atm}}{14.7 \text{ lb f/in}^2}) = 2.22 \frac{\text{atm}}{\text{ft}}$$

$$a = \frac{(2)(2.22 \text{ atm/ft})}{(5.454 \times 10^{-3} \text{ ft}^2)(0.55)(124.74 \text{ lbm/ft}^3)(5 \text{ atm})} = 2.37$$

$$-r_A = 2.5 C_{AO}^{3/2} \frac{(1-X)^{1/2} (2.5-2X)(1-2.37X)^{3/4}}{(1-0.2X)^{3/2}}$$

$$V = F_{AO} \int_0^{0.95} \frac{dX}{-r_A} = \frac{C_{AO} v_o}{2.5 C_{AO}^{3/2}} \int_0^{0.95} \frac{(1-0.2X)^{3/2} dX}{(1-X)^{1/2} (2.5-2X)(1-2.37X)^{3/4}}$$

$$V = (103.98)(0.55) = 57.2 \text{ dm}^3$$

$$\text{Volume of each tube: } V_t = \frac{\pi D^2}{4} L = \frac{\pi}{4} (\frac{1}{12})^2 (20) = 0.109 \text{ ft}^3$$

$$n = \frac{V}{V_t} = (\frac{57.2 \text{ dm}^3}{0.109 \text{ ft}^3})(\frac{1 \text{ ft}}{0.254 \times 12 \text{ dm}})^3 = 19$$

$$b) -r_A = k_2 (C_A^{1/2} C_B - \frac{C_D}{K_e}) ; C_{AO} = \frac{0.2(5)}{0.082(373)} = 0.033 \frac{\text{mol}}{\text{l}}$$

$$k = A e^{-E/RT} \Rightarrow k_2 = k_1 e^{-E/R(1/T_2 - 1/T_1)}$$

CDP4-F (cont'd)

$$k_2 = 2.5 \cdot 10^{-30} \text{ J/mol} / 8.31 \text{ J/mol/K} (1/373 - 1/328) \cdot K^{-1}$$

$$k_2 = 9.43$$

$$-r_A = 9.43 \left(C_{AO}^{3/2} \frac{(1-X)^{1/2} (5/2-2X)}{(1-0.2X)^{3/2}} - 0.1 C_{AO} \frac{2X}{(1-0.2X)} \right)$$

$$-r_A = \frac{9.43 C_{AO}}{(1-0.2X)^{3/2}} \left(C_{AO}^{1/2} (1-X)^{1/2} (5/2-2X) - 0.2X(1-0.2X)^{1/2} \right)$$

At equilibrium $-r_A = 0$

$$(0.033)^{1/2} (1-X_0)^{1/2} (5/2-2X_0) - 0.2X_0 (1-0.2X_0)^{1/2} = 0$$

$$X_0 = 0.664$$

$$\text{FFR } X = 0.70 (0.664) = 0.465$$

$$V = F_{AO} \int_0^X \frac{dX}{-r_A}$$

$$V = C_{AO} v_0 \int_0^X \frac{(1-0.2X)^{3/2} dX}{9.43 C_{AO} \left(C_{AO}^{1/2} (1-X)^{1/2} (5/2-2X) - 0.2X(1-0.2X)^{1/2} \right)}$$

$$V = \frac{50 \text{ dm}^3/\text{min}}{9.43 (1/\text{min})} \int_0^{0.465} \frac{(1-0.2X)^{3/2} dX}{(0.037)^{1/2} (1-X)^{1/2} (5/2-2X) - 0.2X(1-0.2X)^{1/2}}$$

Numerical integration yields

$$V = 3.302 (1.614)$$

$$V = 8.559 \text{ dm}^3$$

$$\text{CSTR } X = 0.85(0.664) = 0.564$$

$$V = \frac{F_{AO}(X-X_0)}{-r_A}$$

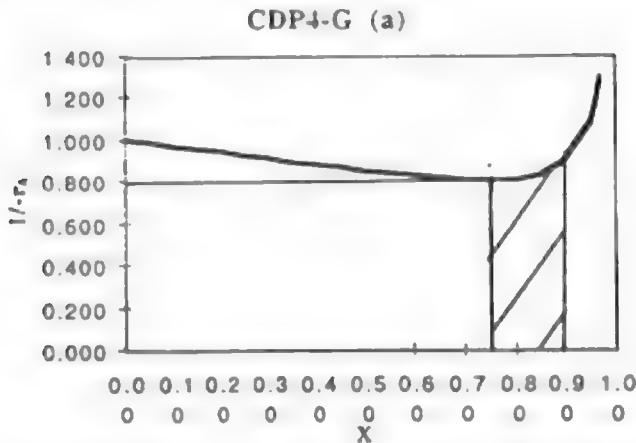
$$V = \frac{C_{AO} v_0 (X-X_0) (1-0.2X)^{3/2}}{9.43 C_{AO} \left(C_{AO}^{1/2} (1-X)^{1/2} (5/2-2X) - 0.2X(1-0.2X)^{1/2} \right)}$$

$$V = \frac{50 \text{ dm}^3/\text{min} (0.564-0.465) (1-0.2(0.564))^{3/2}}{9.43 (0.037)^{1/2} (1-0.564)^{1/2} (5/2-2(0.564)) - 0.2(0.564) (1-0.2(0.564))^{1/2}}$$

$$V = 6.45 \text{ dm}^3$$

CDP4-G

- (a) Plot $1/-r_A$ vs. X to find the optimal system:



From the chart it is apparent that to minimize volume the best system would be a CSTR followed by a PFR.

- (b) To find the volume of the CSTR, calculate the area of the rectangle drawn in the chart and multiply it times the initial flow rate of A:

$$V = (\text{area of rectangle})(F_{A0}) = (0.80)(0.75)(100) = 60 \text{ ft}^3$$

To find the volume of the PFR, calculate the area under the curve between $X=0.75$ and 0.90 , and multiply times the initial flow rate of A:

$$\text{Using the trapezoidal rule: } A = \frac{0.90 - 0.75}{2} (0.885 + 0.800) = 0.126$$

$$V = (\text{area under the curve})(F_{A0}) = (0.126)(100) = 12.6 \text{ ft}^3$$

- (c)

$$\text{Design Equation: } \frac{dX}{dV} = \frac{-r_A}{F_{A0}} \quad \text{or} \quad \frac{dV}{dX} = \frac{F_{A0}}{-r_A}$$

$$\text{Rate Law: } -r_A = \frac{k_1 C_A^{1/2}}{1 + k_2 C_A}$$

$$\begin{aligned} \text{Stoichiometry: } C_A &= C_{A0}(1 - X) \\ C_B &= C_{A0}X \end{aligned}$$

Use these equations in POLYMATH to generate the plot of X , C_A , and C_B vs. V .

Equations:

$$d(v)/d(x) = f_{ao}/r_a$$

$$k_1 = 10$$

$$f_{ao} = 100$$

$$k_2 = 16$$

$$c_{ao} = 0.25$$

$$c_a = c_{ao} \cdot (1-x)$$

$$c_b = c_{ao} \cdot x$$

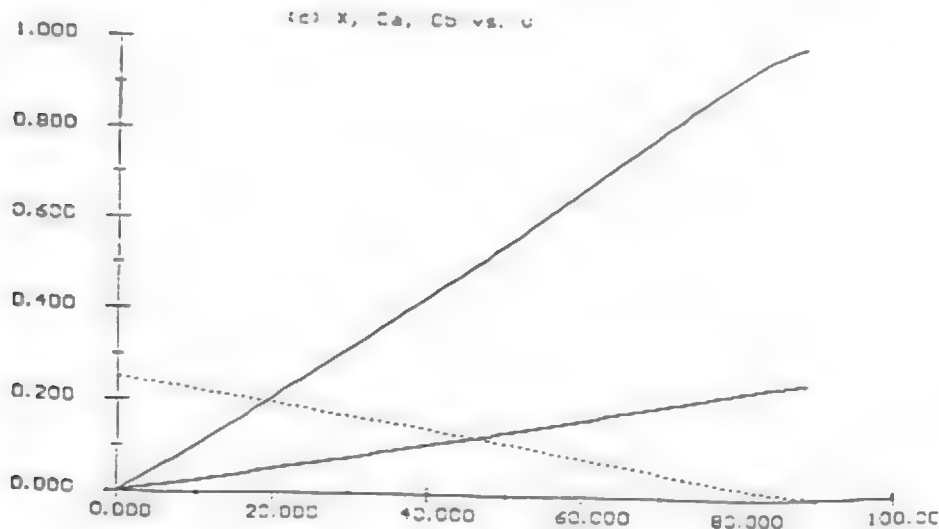
$$r_a = k_1 \cdot c_a^{0.5} / (1 + k_2 \cdot c_a)$$

$$x_0 = 0, \quad x_f = 0.99$$

Initial value

0

<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
x	0	0.99	0	0.99
v	0	89.28	0	89.28
k ₁	10	10	10	10
f _{ao}	100	100	100	100
k ₂	16	16	16	16
c _{ao}	0.25	0.25	0.25	0.25
c _a	0.25	0.25	0.0025	0.0025
c _b	0	0.2475	0	0.2475
r _a	1	1.24994	0.480769	0.480769



CDP4-H

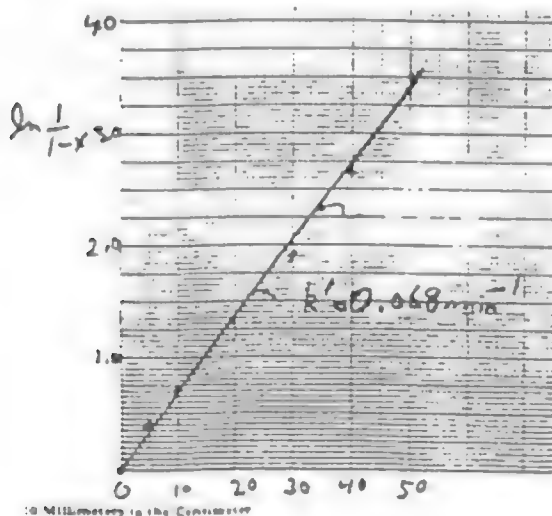
$$N_{A0} \frac{dX}{dt} = V \rho_C (-r'_A) = V \rho_C k C_A$$

$$\text{Liquid Phase } C_A = C_{A0}(1-X) = \frac{N_{A0}}{V}(1-X)$$

$$\frac{dX}{dt} = \rho_C k (1-X)$$

$$\ln \frac{1}{1-X} = \frac{k}{\rho_C} t$$

t	0	5	10	20	30	40	50
X	0	.3	.5	.73	.85	.93	.97
$\ln \frac{1}{(1-X)}$	0	.36	.69	1.31	1.89	2.66	3.5



A plot $\ln \left(\frac{1}{1-X} \right)$ is linear wrt time so we conclude the reaction is first order in 5, 6 benzozoquinoline with $k=0.068 \text{ min}^{-1}$

$$\ln \left[\frac{-r_A(T_2)}{-r_A(T_1)} \right] = \frac{E}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\ln 4 = \frac{E}{R} \left[\frac{1}{353} - \frac{1}{383} \right]$$

$$\frac{E}{R} = \frac{\ln 4}{\frac{30}{(353)(383)}} = 6248 \text{ }^\circ\text{K}$$

$$E = 12,414 \frac{\text{cal}}{\text{mol}}$$

$$\text{at } 90^\circ\text{C} = 363\text{K}$$

$$k(363) = \left[e^{\frac{6248}{373}} \left(\frac{1}{373} - \frac{1}{363} \right) \right] k(373)$$

$$k(363) = 0.63 k(373)$$

4-83

CDP4-H (cont'd)

$$k_2' = \frac{k_2}{k_1} \frac{\rho_{C2} k_1}{\rho_{C1}} = (.63) (2) k_1' = 1.26 k_1'$$

$$k_1' = 0.0857$$

$$\ln \frac{1}{1-X} = k' t$$

$$X = 1 - e^{-k' t}$$

t	0	10	20	30	40	50
X	0	0.57	0.82	0.42	0.97	0.99

CDP4-I



Semibatch

$$N_{B0} = 0.005 \text{ kmol}, C_{B0} = 0.015 \text{ kmol/m}^3, V_0 = 0.33 \text{ m}^3$$

$$C_{A0F} = 0.03 \text{ kmol/m}^3, v = 4 \times 10^{-3} \text{ m}^3/\text{min.}$$

Feed stopped when $V = 0.53 \text{ m}^3$

$$0.33 + 4 \times 10^{-3} t = 0.52$$

$$t = 50 \text{ min}$$

$$a) -r_B = -\frac{r_A}{2} = \frac{k}{2} C_A C_B$$

From $t = 0$ to $t = 50 \text{ min.}$

$$V = V_0 + vt$$

$$C_B = \frac{N_{B0}(1 - X_B)}{V_0 + vt} = \frac{0.005(1 - X_B)}{0.33 + 4 \times 10^{-3} t}$$

$$C_A = \frac{C_{A0F} vt - 2N_{B0} X_B}{V_0 + vt} = \frac{1.2 \times 10^{-4} t - 0.01 X_B}{0.33 + 4 \times 10^{-3} t}$$

$$C_C = C_D = \frac{N_{B0} X_B}{V_0 + vt} = \frac{0.005 X_B}{0.33 + 4 \times 10^{-3} t}$$

$$-r_B V = N_{B0} \frac{dX_B}{dt}$$

$$\frac{k}{2} \frac{(C_{A0F} vt - 2N_{B0} X_B)(N_{B0}(1 - X_B))^{0.5}}{(V_0 + vt)^{0.5}} = N_{B0} \frac{dX_B}{dt}$$

$$\frac{dX_B}{dt} = 6000 \frac{(1.2 \times 10^{-4} t - 0.01 X_B)(0.005(1 - X_B))^{0.5}}{(0.33 + 4 \times 10^{-3} t)^{0.5}}$$

4-84

Plugging that into POLYMATH we get the following table:

Equations:				Initial value
$d(xb)/d(t) = 6000 \cdot (1.2e-4 \cdot t - .01 \cdot xb) \cdot (.005 \cdot (1-xb))^{.5} / (.33 + 4e-3 \cdot t)^{.5}$				0
$Vo = .33$				
$vo = 4e-3$				
$Cb = 0.005 \cdot (1-xb) / (.33 + 4e-3 \cdot t)$				
$ca = (1.2e-4 \cdot t - .01 \cdot xb) / (.33 + 4e-3 \cdot t)$				
$cc = .005 \cdot xb / (.33 + 4e-3 \cdot t)$				
$V = Vo + vo \cdot t$				
$t_0 = 0, \quad t_f = 50$				
t	xb	ca	Cb	cc
0	0	0	0.015151515	0
10	0.11817128	4.9424906e-05	0.011916604	0.0015969092
20	0.23792992	5.0489792e-05	0.0092935376	0.0029015844
30	0.35763903	5.246591e-05	0.0071373441	0.003973767
40	0.47727115	5.5690825e-05	0.0053339679	0.0048701138
50	0.59677332	6.0880811e-05	0.0038040253	0.005629937

after $t = 50$ min, treat as a batch reactor with a volume of 0.53 m^3 and starting conditions:

$$\begin{aligned} N'_{A0} &= C'_{A0} V = (5.7 \times 10^{-4}) \text{ kmol/m}^3 (0.53) \text{ m}^3 = 3.02 \times 10^{-4} \text{ kmol} \\ N'_{B0} &= C'_{B0} V = (40.6 \times 10^{-4}) \text{ kmol/m}^3 (0.53) \text{ m}^3 = 2.15 \times 10^{-4} \text{ kmol} \\ N'_{C0} &= N'_{D0} = (53.8 \times 10^{-4}) \text{ kmol/m}^3 (0.53) \text{ m}^3 = 2.85 \times 10^{-4} \text{ kmol} \end{aligned}$$

Now A is the limiting reactant

$$C_A = \frac{N'_{A0}(1-X_A)}{V_f} = C'_{A0}(1-X_A)$$

$$C_B = \frac{N'_{B0}\left(\theta_s - \frac{X_A}{2}\right)}{V_f} = C'_{B0}\left(\theta_s - \frac{X_A}{2}\right)$$

$$C_C = C_D = \frac{N'_{D0} + N'_{A0} \frac{X_A}{2}}{V_f} = C'_{D0} + C'_{A0} \frac{X_A}{2}$$

$$-r_A = kC_{A0}^{1.5} (1 - X_A) \left(\theta_s - \frac{X_A}{2} \right)^{0.5}$$

$$\theta_s = \frac{40.6}{5.7} = 7.12$$

$$C_{A0} \frac{dX}{dt} = -r_A$$

$$\frac{dX_A}{dt} = 0.143 (1 - X_A) \left(7.12 - \frac{X_A}{2} \right)^{0.5}$$

Plugging into POLYMATH get the following table.

4-I

Equations:

$$d(xa)/d(t) = .143 * (1-xa) * (7.12-xa/2)^{.5}$$

$$cao = 6.09e-5$$

$$cco = .0056$$

$$ca = cao * (1-xa)$$

$$cb = cao * (62.48 - xa/2)$$

$$cc = cco + cao * xa/2$$

$$t_0 = 50, \quad t_f = 68.6$$

4-I

t	xa	ca	cb	cc
50	0	6.09e-05	0.003805032	0.0056
53.1	0.68819307	1.8989042e-05	0.0037840765	0.0056209555
56.2	0.90114376	6.0203448e-06	0.0037775922	0.0056274398
59.3	0.96848514	1.9192549e-06	0.0037755416	0.0056294904
62.4	0.98992685	6.1345493e-07	0.0037748887	0.0056301433
65.5	0.99678108	1.9603251e-07	0.00377468	0.005630352
68.6	0.99897206	6.2601823e-08	0.0037746133	0.0056304187

Now we need to combine the two conversion equations to obtain one equation for the conversion of A, X_A , and another for the conversion of B, X_B .

During the semibatch operation, $X'_B = X_B$. During the batch stage.

$$X'_B = \frac{N_{B0} - N_B}{N_{B0}} = \frac{N_{B0} - C_B V}{N_{B0}}$$

CDP4-I (cont'd)

During the semibatch stage.

$$X'_A = \frac{N_{A_t} - N_A}{N_{A_t}}$$

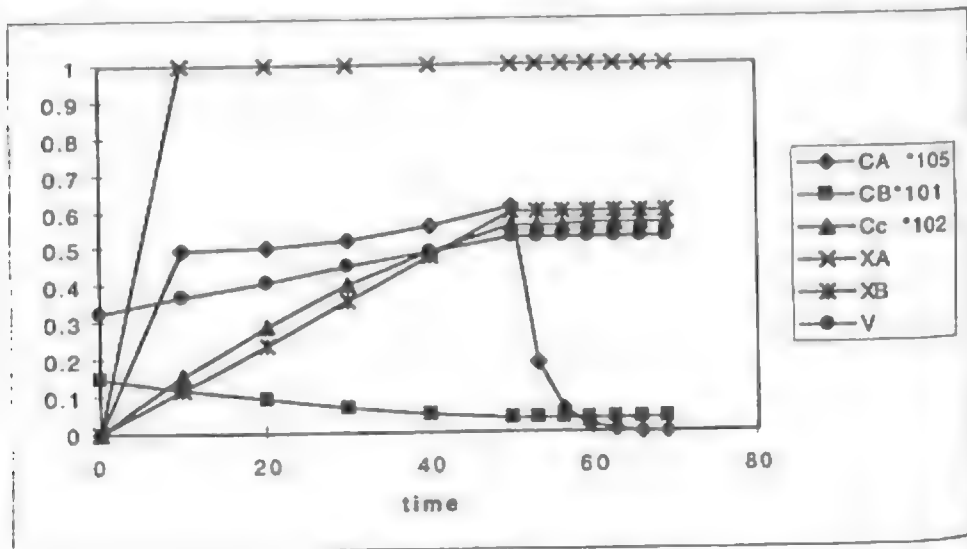
where N_{A_t} is the total amount of A introduced in the reactor by the time t, and N_A is the amount of A left in the reactor at that time, so

$$X'_A = \frac{C_{A0F}v_I - C_A(V_0 + v_I)}{C_{A0F}v_I}$$

During the batch stage.

$$X'_A = \frac{C_{A0F}v_{I0} - C_A V}{C_{A0F}v_{I0}}$$

where t_0 is the time at which the flow of feed was stopped. (i.e. 50 minutes)



t	X _A	X _B
0	0	0
10	0.99847683	0.118
20	0.999139	0.238
30	0.999345	0.358
40	0.9994314	0.477
50	0.99946293	0.597
53.1	0.99983827	0.59932
56.2	0.99995048	0.599532
59.3	0.9999847	0.599744
62.4	0.99999526	0.5998606
65.5	0.99999852	0.5998818
68.6	0.99999954	0.5998924

b) From the table $X_A = 0.97$ at $t = 9.71$ min

c) From the table $X_B = 0.59$ at $t = 49.42$

d) New reaction rate

$$k = k_0 \exp \left[-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]$$

$$k = 6 \exp \left[-\frac{35}{8.3 \times 10^{-3}} \left(\frac{1}{343} - \frac{1}{298} \right) \right]$$

$$= 38.3$$

$$-r_A = k \left(C_A C_B^{0.5} - \frac{C_C^{0.5} C_D^{0.5}}{K} \right), K = 10$$

Semibatch reactor

the concentration equations are the same as before, so, with

$$-r_B = \frac{-r_A}{2}$$

and

$$-r_B V = N_{B0} \frac{dX_B}{dt}$$

$$\frac{k}{2} \left(\frac{(C_{A0} - V_0 X_B)(N_{B0}(1 - X_B))^{0.5}}{(V_0 + V)^{1.5}} - \frac{N_{B0} X_B}{K(V_0 + V)} (V_0 + V) \right) = N_{B0} \frac{dX_B}{dt}$$

$$\frac{dX_B}{dt} = \frac{k}{2} \left[\frac{(C_{A0F}Vt - 2N_{B0}X_B)(N_{B0}(1-X_B))^{0.5}}{N_{B0}(V_0 + Vt)} - \frac{X_B}{K} \right]$$

$$\frac{dX_B}{dt} = 3830 \left(\frac{(1.2 \cdot 10^{-4}t - 0.01X_B)(0.005(1-X_B))^{0.5}}{.033 + 4 \cdot 10^{-3}t} \right) - 1.915 \cdot X_B$$

Recall that in the semibatch reactor stage $X'_B = X_B$

The equation for the conversion of A remains the same as in part a,

$$X'_A = \frac{1.2 \cdot 10^{-4}t - C_A(.033 + 4 \cdot 10^{-3}t)}{1.2 \cdot 10^{-4}t}$$

at equilibrium, $-r_B = 0$

$$C_A C_B^{0.5} = \frac{C_C}{K}$$

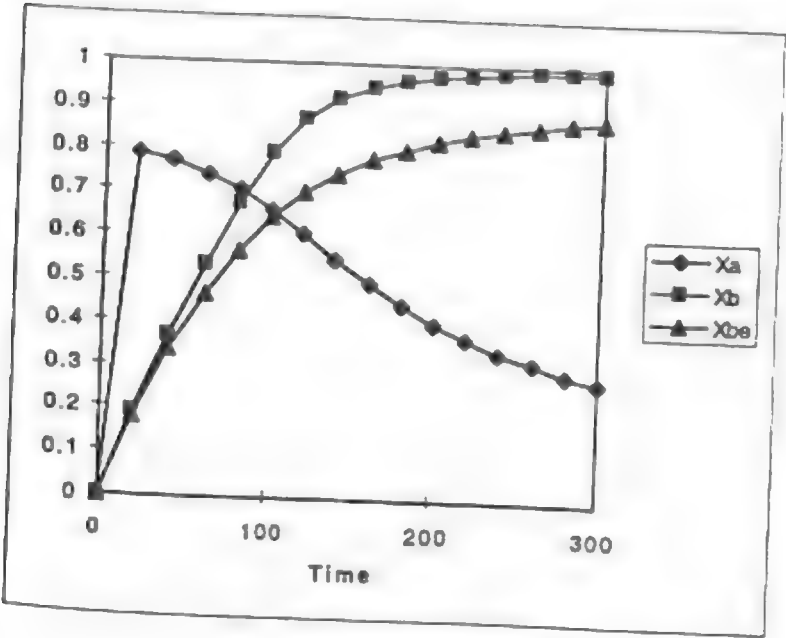
$$K \frac{(C_{A0F}Vt - 2N_{B0}X_{BE})(N_{B0}(1-X_{BE}))^{0.5}}{(V_0 + Vt)^{1.5}} = \frac{N_{B0}X_{BE}}{V_0 + Vt}$$

$$\frac{(C_{A0F}Vt - 2N_{B0}X_{BE})}{(V_0 + Vt)^{0.5}} - \frac{N_{B0}^{0.5}X_{BE}}{K(1-X_{BE})^{0.5}} = 0$$

$$\frac{(1.2 \cdot 10^{-4}t - 0.01X_{BE})}{.033 + 4 \cdot 10^{-3}t} - \left(\frac{0.005}{1-X_{BE}} \right)^{0.5} \frac{X_{BE}}{10} = 0$$

Solving for X_B , X_A and X_{BE} we obtain

t	Xa	Xb	Xbe
0	0	0	0
20	0.788	0.189	0.182
40	0.769	0.369	0.337
60	0.741	0.534	0.464
80	0.705	0.677	0.566
100	0.659	0.791	0.644
120	0.604	0.87	0.702
140	0.547	0.919	0.747
160	0.493	0.947	0.78
180	0.446	0.964	0.805
200	0.406	0.974	0.825
220	0.371	0.981	0.84
240	0.342	0.985	0.853
260	0.317	0.988	0.863
280	0.295	0.99	0.871
300	0.276	0.992	0.878





BATCH

well mixed
no inflow or outflow

1. Mole balance on batch reactor

$$N_{AO} \frac{dX}{dt} = -r_A V$$

$$t = N_{AO} \int_0^X \frac{dX}{-r_A V}$$

2. Rate law

$$-r_A = k C_A C_B$$

3. Stoichiometry

liquid phase $V = V_0$ (batch) [if flow $v = v_0$]

$$C_A = \frac{N_A}{V} = \frac{N_A (1-X)}{V_0} = C_{A0} (1-X)$$

$$C_B = \frac{N_B}{V} = \frac{N_{A0} (\theta_B - \frac{1}{2} X)}{V_0} = C_{A0} (1-X)$$

$$\theta_B = \frac{y_{B0}}{y_{A0}} = \frac{N_{B0}}{N_{A0}} = \frac{C_{B0}}{C_{A0}} = \frac{2}{2} = 1$$

4. Combine

$$-r_A = k C_{A0}^2 (1-X)^2$$

$$t = N_{AO} \int_0^X \frac{dX}{-r_A V} = \frac{N_{AO}}{V_0} \int_0^X \frac{dX}{-r_A} = C_{A0} \int_0^X \frac{dX}{k C_{A0}^2 (1-X)^2}$$

$$t = \frac{1}{k C_{A0}} \int_0^X \frac{dX}{(1-X)^2} = \frac{1}{k C_{A0}} \left[\frac{X}{1-X} \right]$$

Table of reaction integrals can be found in Appendix A-10, p. 725.

a)

$$t = \frac{1}{(0.01 \text{ dm}^3/\text{mol min}) (2 \text{ mol/dm}^3)} \left[\frac{0.9}{1-0.9} \right], \quad t = 450 \text{ min}$$

1. Mole balance on CSTR

$$V = \frac{F_{AO} X}{-r_A}$$

2. Rate Law

$$-r_A = k C_A C_B$$

3. Stoichiometry

liquid phase $v = v_0$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0} = C_{A0}(1-X)$$

$$C_B = \frac{F_B}{v} = \frac{F_{A0}(\theta_B - \frac{1}{2}X)}{v_0} = C_{A0}(1-X)$$

4. Combine

$$V = \frac{F_{A0}X}{k C_{A0}^2 (1-X)^2}$$

5. Parameter evaluation

$$V = \frac{10 \text{ mol/min} (0.9)}{(0.01 \text{ dm}^3/\text{mol min}) (2 \text{ mol/dm}^3)^2 (1-0.9)^2}$$

b) $V = 22500 \text{ dm}^3$

1. Mole balance on PFR

$$F_{A0} \frac{dX}{dV} = -r_A$$

if no pressure or phase change (liquid phase) therefore

$$V = F_{A0} \int_0^X \frac{dX}{-r_A}$$

2. Rate law

$$-r_A = k C_A C_B$$

3. Stoichiometry

liquid phase $v = v_0$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0} = C_{A0}(1-X)$$

$$C_B = \frac{F_B}{v} = \frac{F_{A0}(\theta_B - \frac{1}{2}X)}{v_0} = C_{A0}(1-X)$$

4. Combine

$$-r_A = k C_{A0}^2 (1-X)^2$$

$$V = F_{A0} \int_0^X \frac{dV}{k C_{A0}^2 (1-X)^2} = \frac{F_{A0}X}{k C_{A0}^2} \int_0^X \frac{dX}{(1-X)^2}$$

$$V = \frac{F_{A0}X}{k C_{A0}^2} \left[\frac{X}{1-X} \right]$$

5. Parameter evaluation

$$V = \frac{(10 \text{ mol/min})}{(0.01 \text{ dm}^3/\text{mol min})(2 \text{ mol/dm}^3)^2} \frac{0.9}{1-0.9} =$$

d) Solution similar to part (a) to (c)

$$e) -r_A = k \left[C_A C_B - \frac{C_C}{K_C} \right] \text{ At equilibrium, } -r_A = 0$$

$$K_C = \frac{C_{C_e}}{C_{A_e} C_{B_e}} = \frac{C_{A0} X}{C_{A0}^2 (1-X)^2} = \frac{X}{C_{A0} (1-X)^2}$$

$$K C_{A0} = \frac{2 \text{ dm}^3}{\text{mol}} \times \frac{2 \text{ mol}}{\text{dm}^3} = 4$$

$$1 - 2X + X^2 = \frac{X}{K C_{A0}} = \frac{X}{4}$$

$$X^2 - 2.25 X + 1 = 0$$

$$X_e = 0.61$$

CSTR

$$V = \frac{F_{A0} X}{-r_A} = \frac{F_{A0} X}{k C_{A0} \left[C_{A0} (1-X)^2 - \frac{X}{K_C} \right]}$$

$$X = (0.98) X_e = .60$$

$$V = \frac{(10)(.6)}{(0.01)(2) \left[(2) \left[(1-.6)^2 - \frac{.6}{2} \right] \right]} = 15,000 \text{ dm}^3$$

PFR

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} = k C_{A0} \left[C_{A0} (1-X)^2 - \frac{X}{K_C} \right] = k C_{A0}^2 \left[(1-X)^2 - \frac{X}{K_C C_{A0}} \right]$$

$$= \frac{(0.01)(2)^2}{10} \left[1 - 2X + X^2 - \frac{X}{4} \right]$$

$$V = 250 \int_0^X \frac{dX}{1 - 2.25X + X^2}$$

$$V = 250 \frac{1}{3} [\eta(0) + 4\eta(.15) + 2\eta(.3) + 4\eta(.45) + \eta(.6)] =$$

$$250 \frac{0.15}{3} [1 + 4(1.41) + 2(2.41) + 4(5.26) + 100]$$

$$V = 250 \frac{1}{3} [\eta(0) + 4\eta(.15) + 2\eta(.3) + 4\eta(.45) + \eta(.6)]$$

$$= 250 \frac{0.15}{3} [1 + 4(1.41) + 2(2.41) + 4(5.26) + 100]$$

$$= 1656 \text{ dm}^3$$

CDP4-K

$$V = F_{A1} \int_0^{X_1} \frac{dX}{-r_A}$$

$$-r_A = kC_A$$

$$F_A = F_{A1}(1-X) = F_{A0}[1+R(1-X_0)](1-X)$$

$$v = v_{01}(1+\varepsilon_s X) = v_0[1+R(1+\varepsilon_0 X_0)](1+\varepsilon_s X)$$

$$\varepsilon_s = y_{A0} \delta \left(\frac{1+R(1-X_0)}{1+R(1+\varepsilon_0 X_0)} \right)$$

$$\varepsilon_0 = y_{A0} \delta = 1$$

$$R = 5$$

$$C_A = \frac{F_A}{v} = C_{A0} \left(\frac{[1+R(1-X_0)](1-X)}{[1+R(1+\varepsilon_0 X_0)](1+\varepsilon_s X)} \right)$$

$$F_{A1} = F_{A0} + F_{AR} = F_{A0} + RF_{A0}(1-X_0)$$

Combining:

$$V = \frac{(F_{A0} + F_{A0}R(1-X_0))(1+R(1+X_0))}{1+R(1+X_0)} \int_0^{X_1} \frac{(1-\varepsilon_s X)}{1-X}$$

We also know that $X_s = \frac{X_0}{1+R(1-X_0)}$.

$$F_{A0} = 1 \text{ so } R = 5. \quad \varepsilon_s = y_{A0} \delta \left(\frac{1+R(1-X_0)}{1+R(1+\varepsilon_0 X_0)} \right), \quad \varepsilon_0 = y_{A0} \delta = 1$$

Two equations with two unknowns is solvable and the answer is $X_0 = .495$.

CDP4-L

$$\frac{dP}{dL} = -0.0025$$

$$\frac{dx}{dL} = \frac{-r_A \cdot A}{F_{A0}}$$

$$-r_A = kC_A$$

$$C_A = \frac{F_A}{v_0 P_0} = \frac{F_{A0} P [1+R \cdot (1-x_0)](1-x)}{10 P_0}$$

$$x_0 = \frac{x + Rx}{Rx + 1}$$

Plugging into POLYMATH gets the following:

4.94

CDP4-L cont'd

Equations:

$$d(p)/d(1) = -.0025$$

$$d(x)/d(1) = -ra \cdot A / fao$$

$$A = .02$$

$$fao = .1$$

$$k = .25$$

$$cao = .01$$

$$po = 2$$

$$R = 5$$

$$xo = (x + R \cdot x) / (R \cdot x + 1)$$

$$epss = (1 + R \cdot (1 - xo)) / (1 + R \cdot (1 - xo))$$

$$ca = fao \cdot p / po \cdot (1 + R \cdot (1 - xo)) \cdot (1 - x) / 10$$

$$ra = -k \cdot ca$$

$$l_0 = 0, \quad l_f = 10$$

$$X_0 = .15$$

Initial value

2

0

Variable	Initial value	Maximum value	Minimum value	Final value
1	0	10	7	10
p	2	2	1.975	1.975
a	0	0.0275011	0	0.0275011
A	0.02	0.02	0.02	0.02
fao	0.1	0.1	0.1	0.1
k	0.25	0.25	0.25	0.25
cao	0.01	0.01	0.01	0.01
po	2	2	2	2
R	5	5	5	5
no	0	0.14508	0	0.14508
epss	1	1	0.786307	0.786307
ca	0.04	0.04	0.0304552	0.0304552
ra	-0.015	-0.0126638	-0.015	-0.0126638

CDP4-M

$$\frac{dV}{dX_0} = \frac{F_{A0}}{-r_A}$$

$$-r_A = k C_A C_B$$

$$C_A = \frac{F_A}{v} \quad C_B = \frac{F_B}{v}$$

$$v = v_0 [1 + R(1 + \epsilon_0 X_0)] (1 + \epsilon_S X_S)$$

$$F_A = F_{A0} [1 + R(1 - X_0)] (1 - X_S)$$

$$F_B = F_{A0} [1 + R(1 - X_0)] - F_{A0} [1 + R(1 - X_0)] X_S$$

$$\epsilon_S = \epsilon_0 \left[\frac{1 + R(1 - X_0)}{1 + R(1 + \epsilon_0 X_0)} \right]$$

$$\epsilon_0 = y_{A0} \delta = .5 - 1 = -.5$$

$$R = 4$$

$$X_S = \frac{X_0}{1 + R(1 - X_0)}$$

Plugging into POLYMATH:

4.95

4-m

Equations:

Initial value

$$d(V)/d(x_0) = fao / -ra$$

0

$$k=100$$

$$fao=1$$

$$vo=138.3$$

$$R=4$$

$$epso=-.5$$

$$xs=xo/(1+R*(1-xo))$$

$$eps=epso*(1+R*(1-xo))/(1+R*(1+epso*xo))$$

$$fa=fao*(1+R*(1-xo))*(1-xs)$$

$$fb=fao*(1+R*(1-xo))-fao*(1+R*(1-xo))*xs$$

$$v=vo*(1+R*(1+epso*xo))*(1+eps*xs)$$

$$ca=fa/v$$

$$cb=fb/v$$

$$ra=k*ca*cb$$

$$x_{00} = 0, \quad x_{0f} = 0.5$$

$$V=138 \text{ m}^3$$

Variable	Initial value	Maximum value	Minimum value	Final value
no	0	1.5	0	0.5
v	0	138.015	0	138.015
k	100	.38	100	100
fao	1	1	1	1
vo	138.3	138.3	138.3	138.3
R	4	4	4	4
epso	-0.5	-0.5	-0.5	-0.5
xs	0	0.166667	0	0.166667
eps	-0.5	-0.375	-0.5	-0.375
fa	5	5	2.5	2.5
fb	5	5	2.5	2.5
v	691.5	691.5	510.625	510.625
ca	0.00723065	0.00723065	0.00482044	0.00482144
cb	0.00723065	0.00723065	0.00482044	0.00482144
ra	-0.00522834	-0.00322368	-0.00522824	-0.00322364

CDP4-N

a) Develop new design equation:

$$F_A|_r - F_A|_{r+\Delta r} + hr_A \pi \Delta r$$

$$= \frac{F_A|_{r+\Delta r} - F_A|_r}{\Delta r} + hr_A \pi$$

$$\frac{dF_A}{dr} = hr_A \pi$$

$$F_A = F_{A0}(1 - X)$$

$$F_{A0} \frac{dX}{dr} = -r_A \pi r$$

Then make r_A a function of X and solve.

$$-r_A = k_1 C_A C_B$$

$$C_A = \frac{C_{A0}(1 - X)}{(1 + \epsilon X)}$$

$$C_B = \frac{C_{A0}(\theta_B - X)}{(1 + \epsilon X)}$$

$$\theta_B = 1$$

$$\epsilon = 0$$

$$\frac{dX}{dr} = \frac{kC_{A0}^2(1 - X)^2 \pi r}{F_{A0}}$$

$$\frac{dx}{(1 - X)^2} = \frac{kC_{A0}^2 \pi r dr}{F_{A0}}$$

$$\frac{X}{1 - X} = \frac{kC_{A0}^2 \pi r^2}{2F_{A0}}$$

$$X = \frac{kC_{A0}^2 \pi r^2}{2F_{A0}} - \frac{kC_{A0}^2 \pi r^2 X}{2F_{A0}}$$

$$X(1 - \frac{kC_{A0}^2 \pi r^2}{2F_{A0}}) = \frac{kC_{A0}^2 \pi r^2}{2F_{A0}}$$

$$X = \frac{\frac{kC_{A0}^2 \pi r^2}{2F_{A0}}}{1 - \frac{kC_{A0}^2 \pi r^2}{2F_{A0}}}$$

b) Now with pressure drop

$$\frac{dX}{dr} = \frac{-r_A \pi r dr}{F_{A0}}$$

$$r_A = -k C_A C_B$$

$$C_A = C_B = C_{A0}(1-X)y$$

$$y = (1-\alpha W)^{0.5}$$

$$W = \rho_s \pi (r - r_0)^2 h$$

Plugging this into POLYMATH, the following graph is made:

4-9

Equations:

$$d(x)/d(r) = -r_a * 3.1416 * r^2 * h / f_{a0}$$

$$h = 0.01$$

$$h = 0.4$$

$$f_{a0} = 10$$

$$c_{a0} = 0.1$$

$$\alpha = 0.07$$

$$r_0 = 2$$

$$r_0 = 1$$

$$W = r_0 * 3.1416 * (r - r_0)^2 * h$$

$$y = 1$$

$$y = (1 - \alpha * W)^{0.5}$$

$$c_a = c_{a0} * (1 - x) * y$$

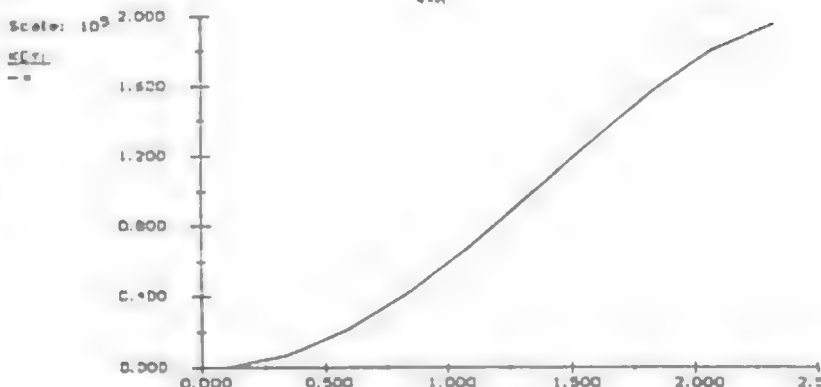
$$c_b = c_a$$

$$r_a = k * c_a * c_b$$

$$r_0 = 0.1, \quad r_f = 10$$

Initial value

0



c) Increasing the value for k increases the conversion, while decreasing it decreases the conversion. Increasing F_{A0} will decrease the conversion and decreasing it will increase the conversion. Increasing C_{A0} causes a dramatic increase of conversion. Similarly, decreasing C_{A0} results in a large decrease in conversion. Increasing the height will only slightly increase the conversion and a decrease in height causes only a small decrease in conversion. Increasing R_0 decreases the volume of the reactor, therefore decreasing conversion. Increasing R_1 will increase the conversion as volume increases.

CDP4-O

a)



$$X_0 = .1 \text{ g/dm}^3$$

$$S_0 = 50 \text{ g/dm}^3$$

$$V = 5 \text{ dm}^3$$

$$Y = .5 \text{ g cell formed/g substrate consumed}$$

Cell balance,

Accumulation = In - Out + generation
No flow terms

$$\frac{d(VX)}{dt} = \mu VX$$

Constant volume,

$$\frac{dX}{dt} = \mu X \quad (1)$$

$$\frac{dX}{dt} = \frac{\mu_{\max} S}{K_s + S} X \quad (2)$$

Substrate balance,

$$\frac{d(VS)}{dt} = - \frac{\mu VX}{Y} - m VX$$

growth maintenance

Constant volume,

$$\frac{dS}{dt} = \frac{\mu X}{Y} - m X \quad (3)$$

$$\frac{dS}{dt} = \frac{-\mu_{\max} S X}{(K_s + S) Y} - m X \quad (4)$$

growth rate (μ)
growth rate (μ)

b) In order to do this exactly, one would have to solve equations (3) and (4) simultaneously. This could be done numerically. However, the growth rate μ is essentially constant except when the substrate concentration becomes very small:

CDP4-O(cont'd)

μ	S
.8298 hr ⁻¹	50 g/l
.8292	10
.8283	5
.8218	1
.692	.05

As a first approximation, let $\mu = \mu_{\max} = .83 \text{ hr}^{-1}$ and solve equation (1). It can then be determined from Eq. (3) whether the substrate concentration is indeed still high enough to justify the approximation that $\mu = \mu_{\max}$.

From (1),

$$\int_{X_0}^X \frac{dX}{X} = \mu_{\max} \int_0^t dt$$

$$\ln \frac{X}{X_0} = \mu_{\max} t \quad \text{or} \quad X = X_0 e^{\mu_{\max} t}$$

$$t = \frac{\ln(20/.1)}{.83}$$

$$t = 6.38 \text{ hr}$$

From (3),

$$\frac{dS}{dt} = - \left(\frac{\mu_{\max}}{Y} + m \right) X$$

$$\int_{S_0}^S dS = - \left(\frac{\mu_{\max}}{Y} + m \right) X_0 \int_0^t e^{\mu_{\max} t} dt$$

$$S - S_0 = - \left(\frac{\mu_{\max}}{Y} + m \right) X_0 \left. \frac{e^{\mu_{\max} t}}{\mu_{\max}} \right|_0^t$$

$$S = S_0 - \left(\frac{\mu_{\max}}{Y} + m \right) \frac{X_0}{\mu_{\max}} (e^{\mu_{\max} t} - 1) \quad (5)$$

At $t = 6.38 \text{ hr}$

$$S = 50 - \left(\frac{.83}{.5} + .1 \right) \left(\frac{1}{.83} \right) (.83)(6.38) - 1$$

$$= 7.93 \text{ g/l}$$

4-100

CDP4-O (cont'd)

From Eq. (4) part d),

$$X = \frac{(F/V)(S_0 - S)}{(\mu_{\max} S / (K_S + S)Y) + m}$$

Substitute the relation for S into the above equation. After some algebra,

$$X = \frac{Y S_0 \mu_{\max} \tau - Y(S_0 + K_S) \tau^2}{\mu_{\max} m Y + (\mu_{\max} - m Y) \tau - \tau^2}$$

where

$$\tau = \frac{F}{V}$$

To find the maximum cell concentration, differentiate and set equal to zero:

$$\frac{dX}{d\tau} = \frac{[\mu_{\max} m Y + (\mu_{\max} - m Y) \tau - \tau^2] [Y S_0 \mu_{\max} - 2Y(S_0 + K_S) \tau] - [Y S_0 \mu_{\max} \tau - Y(S_0 + K_S) \tau^2] [\mu_{\max} - m Y - 2\tau]}{[\mu_{\max} m Y + (\mu_{\max} - m Y) \tau - \tau^2]^2}$$

Set equal to zero. The only unknown is τ . After some algebra,

$$0 = \frac{.496 \tau^2 - .8304 \tau + .34445}{(.0415 + .78\tau - \tau^2)^2}$$

$$0 = .496 \tau^2 - .8304 \tau + .34445$$

Solving with the quadratic equation:

$$\tau = .9163, .7579$$

These corresponding flow rates are 91.63 l/hr, 75.79 l/hr. The 91.63 l/hr flow rate is a meaningless solution because this is greater than the maximum allowable flow rate (part e).

∴ At $F = 75.79$ l/hr, the cell concentration is maximum.

The maximum cell concentration can be calculated using $\tau = .7579$.

$$X = \frac{Y S_0 \mu_{\max} \tau - Y(S_0 + K_S) \tau^2}{\mu_{\max} m Y + (\mu_{\max} - m Y) \tau - \tau^2}$$

$$X_{\max} = 9.324 \text{ g/l}$$

$$F = 75.79 \text{ l/hr}$$

4-101

CDP4-O (cont'd)

At this substrate concentration, the actual growth rate is:

$$\mu = \frac{.83(7.93)}{.01 + 7.93}$$

$$= .8290 \text{ hr}^{-1}$$

The approximation that $\mu = \mu_{\max} = .83 \text{ hr}^{-1}$ at all times is indeed valid.

c) Divide Equations (2) and (4) from part (b).

$$\frac{dS}{dX} = \frac{(-\mu_{\max} SX / (K_S + S) Y) - m X}{(\mu_{\max} SX / K_S + S) Y}$$

After some algebraic manipulation,

$$\frac{dS}{dX} = \frac{-mK_S Y - (\mu_{\max} + mY) S}{\mu_{\max} Y S}$$

$$\int_{S_0}^S \frac{S}{mK_S Y + (\mu_{\max} + mY) S} dS = \frac{-1}{\mu_{\max} Y} \int_{X_0}^X dX$$

From table of integrals,

$$\int \frac{X dX}{a + bX} = \frac{X}{b} - \frac{a}{b^2} \ln(a + bX)$$

Integrating,

$$\frac{S - S_0}{\mu_{\max} + mY} - \frac{mK_S Y}{(\mu_{\max} + mY)^2} \ln \frac{[mK_S Y + (\mu_{\max} + mY)S]}{[mK_S Y + (\mu_{\max} + mY)S_0]} = \frac{X_0 - X}{\mu_{\max} Y}$$

The max. cell concentration will occur when all the substrate is consumed

(i.e. $S=0$).

$$\frac{-50}{.83 + (.1)(.5)} - \frac{(.1)(.01)(.5)}{[.83 + (.1)(.5)]^2} \ln \frac{(.1)(.01)(.5)}{(.1)(.01)(.5) + (.88)(50)} = \frac{X_0 - X}{(.83)(.5)}$$

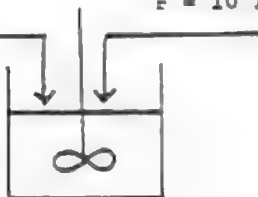
Solving for X ,

$$X = 23.69 \text{ g/l}$$

$$d) S_0 = 20 \text{ g/l}$$

$$F = 10 \text{ l/hr}$$

$$F = 10 \text{ l/hr}$$



$$V = 100 \text{ l}$$

4-102

CDP4-O (cont'd)

From Eq. (4) part d),

$$X = \frac{(F/V)(S_0 - S)}{(\mu_{\max} S / (K_S + S)Y) + m}$$

Substitute the relation for S into the above equation. After some algebra,

$$X = \frac{YS_0\mu_{\max}\tau - Y(S_0 + K_S)\tau^2}{\mu_{\max}mY + (\mu_{\max} - mY)\tau - \tau^2}$$

where

$$\tau = \frac{F}{V}$$

To find the maximum cell concentration, differentiate and set equal to zero:

$$\frac{dX}{d\tau} = \frac{[\mu_{\max}mY + (\mu_{\max} - mY)\tau - \tau^2][YS_0\mu_{\max} - 2Y(S_0 + K_S)\tau] - [YS_0\mu_{\max}\tau - Y(S_0 + K_S)\tau^2][\mu_{\max} - mY - 2\tau]}{[\mu_{\max}mY + (\mu_{\max} - mY)\tau - \tau^2]^2}$$

Set equal to zero. The only unknown is τ . After some algebra,

$$0 = \frac{.496\tau^2 - .8304\tau + .34445}{(.0415 + .78\tau - \tau^2)^2}$$

$$0 = .496\tau^2 - .8304\tau + .34445$$

Solving with the quadratic equation:

$$\tau = .9163, .7579$$

These corresponding flow rates are 91.63 l/hr, 75.79 l/hr. The 91.63 l/hr flow rate is a meaningless solution because this is greater than the maximum allowable flow rate (part c).

∴ At $F = 75.79$ l/hr, the cell concentration is maximum.

The maximum cell concentration can be calculated using $\tau = .7579$,

$$X = \frac{YS_0\mu_{\max}\tau - Y(S_0 + K_S)\tau^2}{\mu_{\max}mY + (\mu_{\max} - mY)\tau - \tau^2}$$

$$X_{\max} = 9.324 \text{ g/l}$$

$$F = 75.79 \text{ l/hr}$$

4-103

CDP4-P Given: $A + B \rightarrow C + D$ is a tubular reactor:



$$\begin{aligned} \dot{M}_A &= 210 \text{ lb/hr} & X &= 0.50 \\ \dot{M}_B &= 260 \text{ lb/hr} \end{aligned}$$

$$F_{AC} = \frac{\dot{M}_A}{(M_w)_A} = \frac{210 \text{ lb/hr}}{\frac{139 \text{ lb}}{\text{lbmole}}} = 1.51 \text{ lbmole/hr}$$

$$F_{BO} = \frac{\dot{M}_B}{(M_w)_B} = \frac{260 \text{ lb/hr}}{\frac{172 \text{ lb}}{\text{lbmole}}} = 1.51 \text{ lb/lbmole/hr}$$

$$\theta_B = \frac{F_{BO}}{F_{AO}} = 1$$

For a tubular reactor:

$$V = F_{AO} \int_0^X \frac{dX}{-r_A} \quad -r_A = k C_A C_B$$

No volume changes on mixing: $v = 0$; $C_{AO} = C_{BO}$:

$$\therefore -r_A = k C_{AO}^2 [1-X]^2; \quad V = F_{AO} \int_0^X \frac{dX}{k C_{AO}^2 [1-X]^2} = \frac{F_{AO} X}{k C_{AO}^2 (1-X)}$$

$$\text{or, solving for } k, \quad k = \frac{X F_{AO}}{C_A^2 V (1-X)} = \frac{v_o X}{C_{AO} V (1-X)}$$

$$v_o = \frac{\dot{M}_A}{M_A} + \frac{\dot{M}_B}{M_B} = \frac{210 \text{ lb/hr}}{47.8 \text{ lb/ft}^3} + \frac{260 \text{ lb/hr}}{54.0 \text{ lb/ft}^3}$$

$$v_o = 4.39 \text{ ft}^3/\text{hr} + 4.82 \text{ ft}^3/\text{hr} = 9.21 \text{ ft}^3/\text{hr}$$

$$\therefore C_{AO} = F_{AO}/v_o = \frac{1.51 \text{ lbmole/hr}}{9.21 \text{ ft}^3/\text{hr}} = 0.164 \text{ lbmole/ft}^3$$

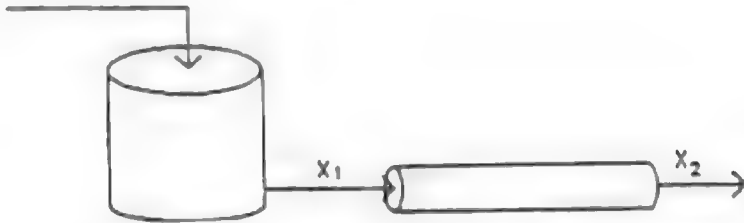
$$\therefore k = \frac{9.21 \text{ ft}^3/\text{hr} (0.5)}{0.164 \text{ lbmole/ft}^3 \times 5.33/\text{ft}^3 (1-0.5)} = \frac{10.55 \text{ ft}^3}{\text{lbmole-hr}}$$

4-104

CDP4-P (cont'd)

Alternative scheme - same feed as before

$$F_{AO} = F_{DC} = 2.51 \text{ lbmole/hr}$$



$$V = V_{CSTR} = \frac{100 \text{ gal} \times 1 \text{ ft}^3}{7.48 \text{ gal}} = 13.37 \text{ ft}^3 = \frac{F_{AO} X_1}{-r_A} = \frac{F_{AO} X_1}{k C_{AO}^2 (1-X_1)^2}$$

$$V = \frac{v_o X_1}{k C_{AO} (1-X_1)^2}$$

$$\text{or: } X_1^2 - \left[2 + \frac{v_o}{k C_{AO} V}\right] X_1 + 1 = 0$$

$$X_1 = \frac{\left[2 + \frac{v_o}{k C_{AO} V}\right] \pm \left[\left(2 + \frac{v_o}{k C_{AO} V}\right)^2 - 4\right]^{1/2}}{2} = \frac{1.075}{2} = 0.533$$

$$V_{PF} = F_{AO} \int_{X_1}^{X_2} \frac{dX}{k C_{AO}^2 (1-X)^2} = \frac{v_o}{k C_{AO}} \int_{X_1}^{X_2} \frac{dX}{(1-X)^2} = \frac{v_o}{k C_{AO}} \left[\frac{1}{1-X_2} - \frac{1}{1-X_1} \right]$$

$$\frac{1}{1-X_2} = \frac{1}{1-X_1} + \frac{k C_{AO} V_{PF}}{v_o} = \frac{1}{1-0.533} + \frac{(10.55)(.164)(5.33)}{(9.21)}$$

$$\frac{1}{1-X_2} = 2.16 + 1; \quad X_2 = 1 - \frac{1}{3.16} = .684$$

CDP4-O

a)

From the mole balance for H_2SO_4 :

$$F_B - 0 + 0 = \frac{dN_B}{dt}$$

$$N_B = 10t$$

Concentration:

$$\frac{F_B}{V} = \frac{dC_B}{dt}$$

$$V = V_0 + v_0 t$$

$$\frac{F_B dt}{V_0 + v_0 t} = dC_B$$

Integrating:

$$C_B = \frac{F_B}{v_0} \ln \left(\frac{V_0 + v_0 t}{V_0} \right)$$

For species A mole balance:

$$0 - 0 + r_A V = \frac{dN_A}{dt}$$

$$-r_A = k C_A C_B$$

$$C_A = \frac{N_A}{V}$$

$$C_B = \frac{F_B}{v_0} \ln \left(\frac{V_0 + v_0 t}{V_0} \right)$$

$$-k N_A \frac{F_B}{v_0} \ln \left(\frac{V_0 + v_0 t}{V_0} \right) = \frac{dN_A}{dt}$$

For Concentration:

$$0 - 0 + r_A V = \frac{dN_A}{dt}$$

$$r_A = \frac{dC_A}{dt}$$

$$-r_A = k C_A C_B$$

$$C_B = \frac{F_B}{v_0} \ln \left(\frac{V_0 + v_0 t}{V_0} \right)$$

$$-k C_A \frac{F_B}{v_0} \ln \left(\frac{V_0 + v_0 t}{V_0} \right) = \frac{dC_A}{dt}$$

CDP4-Q (cont'd)

b) From POLYMATH, the answer comes out this way

Equations	Variable	Initial value	Maximum value	Minimum value	Final value
$d(ca)/dt = ra$	t	0	30	3	30
$k=0.05$	ca	10	10	1.35676	2.05676
$fb=10$	k	0.05	0.05	0.05	0.05
$vo=5$	fb	10	10	10	10
$Vo=100$	vo	5	5	5	5
$V=Vo+vo*t$	Vo	100	100	100	100
$cb=fb/vo*\ln((Vo+vo*t)/Vo)$	V	100	250	100	250
$ra=-k*ca*cb$	cb	0	1.81258	0	1.81258
$t_0 = 0, \quad t_f = 30$	ra	-3	-3	-0.356348	-0.182459

c) Species A:

$$0 - 0 + r_A V = \frac{dN_A}{dt}$$

$$r_A = \frac{dC_A}{dt}$$

$$-r_A = k C_A C_B - \frac{C_C}{K_c}$$

$$C_B = \frac{F_B}{V_0} \ln \left(1 + \frac{v_0 t}{V_0} \right)$$

Species C

$$0 - 0 + r_C = \frac{dC_C}{dt}$$

$$r_C = k C_A C_B - \frac{C_C}{K_c}$$

$$C_B = \frac{F_B}{V_0} \ln \left(1 + \frac{v_0 t}{V_0} \right)$$

Plugging into POLYMATH gives the following graph:

Equations:

$$d(ca)/dt = ra$$

$$d(cc)/dt = rc$$

$$k=0.05$$

$$ke=2$$

$$fb=10$$

$$vo=5$$

$$Vo=100$$

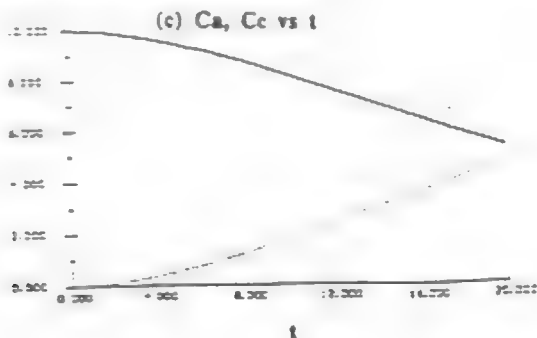
$$cb=fb/vo*\ln(1+vo*t/Vo)$$

$$ra=-k*(ca*cb-cc/ke)$$

$$rc=-ra$$

$$t_0 = 0, \quad t_f = 20$$

Key
— Ca
... Cc



4-107

CDP4-Q (cont'd)

d) The concentration of A will never get very high for the irreversible part because as soon as it enters the reactor it reacts. For the irreversible part it will increase and the concentration of C will also increase.

e) Species B (H_2SO_4):

$$0 - 0 - 0 = \frac{dN_B}{dt}$$

$$N_B = N_{B0}$$

$$C_B = \frac{N_{B0}}{V_0 + v_0 t}$$

Species A:

$$10 - 0 + r_A V = \frac{dN_A}{dt}$$

$$-r_A = k C_A$$

$$C_A = \frac{N_A}{V}$$

$$10 - k N_A = \frac{dN_A}{dt}$$

$$\frac{dN_A}{10 - k N_A} = dt$$

$$-\frac{1}{k} [\ln(10 - k N_A) - \ln(10 - k N_{A0})] = t$$

$$\ln\left(\frac{10 - k N_A}{10 - k N_{A0}}\right) = -kt$$

$$\frac{10 - k N_A}{10 - k N_{A0}} = e^{-kt}$$

$$N_A = \frac{10 - e^{-kt}(10 - k N_{A0})}{k}$$

$$C_A = \frac{N_A}{V_0 + v_0 t}$$

After 30 min the concentration is 0.44 mol/dm^3

Equations:

$$d(n_A)/d(t) = 10 - r_A V$$

$$d(n_C)/d(t) = r_C V$$

$$k = 0.5$$

$$K_C = 2$$

$$V_0 = 200$$

$$v_0 = 5$$

$$V = V_0 + v_0 t$$

$$C_A = n_A / V$$

$$C_C = n_C / V$$

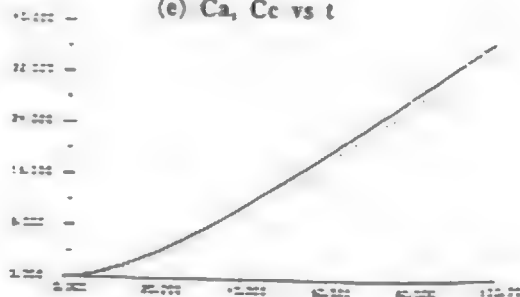
$$r_A = -k \cdot C_A \cdot C_C / K_C$$

$$r_C = k \cdot C_A \cdot C_C / K_C$$

$$t_0 = 0, \quad t_f = 100$$

(e) C_A, C_C vs t

Key
 — C_A
 --- C_C



4-108

Chapter 5

General: In Chapters 3 and 4, the students were given the rate law. The problems in this chapter reinforce how to obtain the rate law from experimental data.

P5-1. An open-ended problem that requires students to create and original problem and solution.

P5-2. "What if. . ." problem.

Problems P5-3, P5-5, P5-7, and P5-18 all involve batch reactor experiments to find the reactor order and specific reaction rate. The students can use different techniques to differential the data or can use regression. These problems can be alternated from year to year.

P5-4. This problem usually trips up some students because many go blindly ahead and differentiate the data (dC_A/dt) not realizing the data were taken in a CSTR at steady state.

P5-6. Differentiate the data down a PFR to find the rate law parameters. Note the reaction is reversible. Quite tricky and time consuming.

P5-8. California Exam Problem where one first needs to determine in the rate law parameters from a batch experiment. Part (a) is quite straight forward but part (b) usually trips the students. Good problem. Requires thinking and not just choosing a formula.

P5-9. Straight forward problem involving the method of half lives.

P5-10. Good problem involving regression AND thinking. May be time consuming if the students don't get the hint and see it is the sum of two rate laws, zero and first order.

P5-11. Very short problem once the students realize the % decomposition is the same for different entering concentrations. No calculation is necessary to determine the reaction order.

P5-12. Fairly straight forward problem to determine the reaction order and specific reaction rate. Shows the application of CRE principles to the electronics industry.

Problems P5-13, P5-14, P5-15, P5-19, P5-20, and P5-21 are straight forward problems using nonlinear regression. They can be alternated from year to year.

P5-16. Shows an important concept where lumping of reactants is used to model first and second order reactions.

P5-17. A problem on designing experiments.

P5-18. Can be used alternatively with P5-3, P5-5, and P5-8.

CDP5-A Alternative to problems P5-3, P5-5, and P5-7. Read data.

CDP5-B Alternative to P5-6, but simpler.

CDP5-C Fairly difficult problem. Usually assigned at the graduate level.

CDP5-D Alternative to P5-9.

CDP5-E More difficult to alternative P5-7.

Summary

	<u>Assigned</u>	<u>Alternates</u>	<u>Difficulty</u>	<u>Time</u>	<u>Solution Given</u>
P5-1				60	No
P5-2				15	No
P5-3	AA	5,7,8,18,A,B,C,E	SF	30	Yes
● P5-4			SF	20	Yes
● P5-5	AA	3,7,8,18,A,B,C	SF	20	No
P5-6	G		SF	60	Yes
P5-7	AA	3,5,8,18,A,B,C,E		40	Yes
● P5-8		3,5,7,18,A,B,C,E		40	Yes
P5-9	I	D		25	Yes
P5-10	AA	13,14,15,19,20,21		60	Yes
P5-11	O			15	Yes
P5-12	I			60	Yes
P5-13	AA	10,14,18,19,20,21		30	Yes
P5-14	AA	10,13,18,19,20,21		45	Yes
P5-15	G			40	Yes
P5-16	G			60	Yes
P5-17	G			(a) 40	Yes
P5-18	AA	3,5,7,8,A,B,C,E		60	Yes
● P5-19	AA	10,13,14,15,20,21		45	Yes
P5-20	AA	10,13,14,15,19,21		45	Yes
P5-21	AA	10,13,14,15,19,20		30	Yes
CDP5-A		5,7,8,18,B,C,E		30	Yes
CDP5-B		5,7,8,18,A,C,E		45	Yes
CDP5-C		5,7,8,18,A,B,E		60	Yes
CDP5-D		5-9		20	Yes
CDP5-E		5,7,8,18,A,B,C		60	Yes

Assigned

- = Always assigned, AA = Always assign one from the group of alternates,
- O = Often, I = Infrequently, S = Seldom, G = Graduate level

Alternates

In problems that have a dot in conjunction with AA means that one of the problems, either the problem with a dot or any one of the alternates are always assigned.

Time

Approximate time in minutes it would take a B/B* student to solve the problem.

Difficulty

- SF = Straight forward reinforcement of principles (plug and chug)
- FSF = Fairly straight forward (requires some manipulation of equations or an intermediate calculation).
- IC = Intermediate calculation required
- M = More difficult
- OE = Some parts open-ended.

Note the letter problems are found on the CD-ROM. For example A = CDP1-A.

Summary Table Ch-5

	Reasoning	Graphical, Numerical Polynomial Analysis	Method of Half Lines	Regression
Straight Forward	4,11	3,5,6,7,8,12,18	9	5
Fairly Straight Forward		A	D	13,19,20,21
More Difficult	16	C,E		10,14,15
Critical Thinking	17	3(b,c),4(c),5(b), 7(c,d),8(c)		14(b),16(a), 18(d)

Chapter 5

P5-1 No solution will be given.

P5-2 No solution will be given.

P5-3

$$-r_A = kC_A^\alpha = -\frac{dC_A}{dt}$$

Time (min)	C_A (mol/dm ³)	$-\Delta C_A/\Delta t$	$-dC_A/dt$
0	4		0.39
3	2.89	0.37	0.35
5	2.25	0.32	0.30
8	1.45	0.267	0.25
10	1	0.225	0.21
12	0.65	0.175	0.15
15	0.25	0.133	0.1
17.5	0.07	0.072	0.06

Plot of $\log -dC_A/dt$ vs $\log C_A$ shows $\alpha = 0.5$

$$k_A = \frac{-\frac{dC_A}{dt}}{C_A^{0.5}} = \frac{.15}{0.65^{0.5}} = 0.19 \frac{\text{mol}^{0.5}}{\text{dm}^{1.5} \text{ min}}$$

P5-4

a)

$$\frac{C_{A0} - C_A}{\tau} = kC_A^\alpha$$

$$\ln\left(\frac{C_{A0} - C_A}{\tau}\right) = \ln k + \ln C_A$$

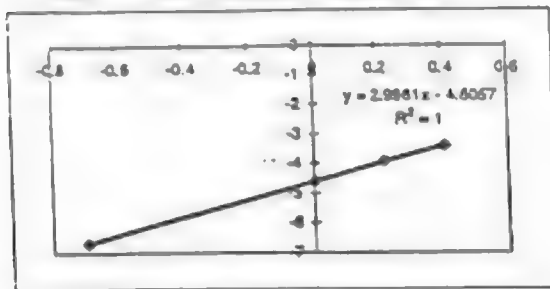
Plotting $\ln\left(\frac{C_{A0} - C_A}{\tau}\right)$ vs. $\ln C_A$

5-4

P5-4 cont'd

Problem 5-4

space time	Ca	ln(Ca)	ln((Cao-Ca)/A)
15	1.5	0.405465	-3.40119738
38	1.25	0.223144	-3.92526823
100	1	0	-4.60517019
1200	0.5	-0.69315	-6.68461173



$\alpha = \text{slope} = 3$
 $\ln k = \text{intercept} = -4.6$
 $k = 0.01$

P5-5

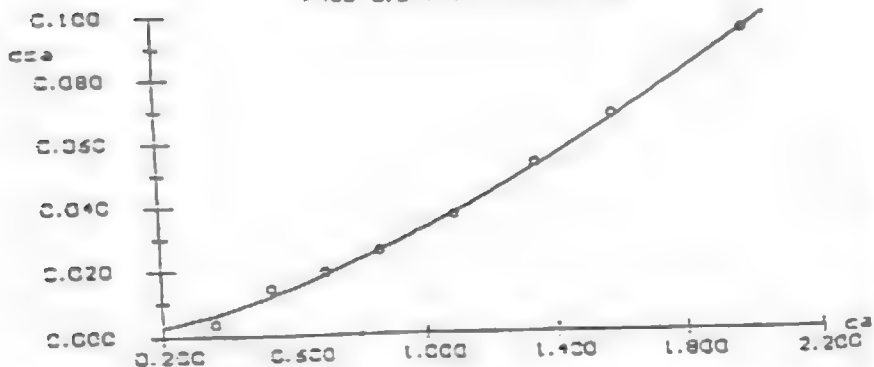
$$\frac{dC_A}{dt} = kC_A^n$$

From a non-linear fit, we get

$$k = 0.033$$

$$n = 1.54$$

P5-5 (non linear fit)



Model: $C_A = k \cdot t^{1.54}$

$$k = 0.0326929$$

$$n = 1.53935$$

4 positive residuals, 4 negative residuals. Sum of squares = 1.49367e-04

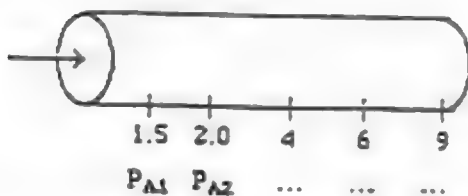
5-5

$AsH_1 = 1.5$	Z	P	$-\frac{dP}{dZ}$
	0	129	45.3
	1.5	70	28.63
	2.5	50	19.4
	4.0	30	9.5
	6.5	18	1.3
	9.0	16	(1.7)

$AsH_3 = 3.0$	Z	P	$-\frac{dP}{dZ}$
	0	129	90
	1.5	45	34.0
	2.5	22	15.4
	4.0	10	2.0

$AsH_3 = 3.0$	Z	P	$-\frac{dP}{dZ}$
	0	129	17.4
	1.5	95	15.0
	2.5	85	13.3
	4.0	80	10.8
	6.5	42	6.2
	9.0	40	1.3

PFR



Task 1. Rewrite the design equation (i.e., mole balance) in terms of the measurement variables. Recall $V = A_C Z$, then

$$\frac{dX}{dZ} = \frac{-r_A A_C}{F_{A0}}$$

56

5-6 cont'd

For isothermal operation and no pressure drop.

$$C_A = C_{A0} \frac{(1-X)}{(1+\epsilon X)} \quad C_A = P_A/RT$$

$$P_A = P_{A0} \frac{(1-X)}{(1+\epsilon X)}$$

$$(1+\epsilon X) P_A = P_{A0} (1-X)$$

$$X = \frac{1 - P_A/P_{A0}}{1 + \epsilon X P_A/P_{A0}}$$

$$\frac{d \left[1 - P_A/P_{A0} \right]}{dZ \left(1 + \epsilon \frac{P_A}{P_{A0}} \right)} = \frac{-r_A A_C}{F_{A0}}$$

Now we have the differential mole balance in terms of the measured variables P_A and Z .

Postulate

$$-r_A = k \left[P_A^\alpha P_B^\beta - \frac{P_C^\gamma}{K_p} \right]$$

Task 2. Look for simplifications.

A) See if volume change can be neglected.

$$\epsilon = y_{A5} \delta = \frac{0.129}{152} (-1) = (8 \times 10^{-4}) - 0$$

$\epsilon \equiv 0$ therefore neglect volume change.

$$\text{Then: } -\frac{dP_A}{dZ} = \frac{\overbrace{P_{A0} k A_C}^{\kappa'}}{F_{A0}} \left[P_A^\alpha P_B^\beta - \frac{P_C^\gamma}{K_p} \right]$$

B) We see that for runs 1 and 3 where $P_{A5H_1} = 1.5$ and 3.0 torr, respectively, that most of the Et_3In is consumed, indicating the equilibrium is reasonably far to the right. Consequently, the reverse reaction is negligible in the first part of the reactor, i.e.,

$$-r_A = k' P_A^\alpha P_B^\beta$$

C) We also see that for runs 1 and 3 that B is in excess and that for excess B

$$-r_A = k' P_{B0}^\beta P_A^\alpha = k'' P_A^\alpha$$

$$-\frac{dP_A}{dZ} = k'' P_A^\alpha$$

Algorithm

5-7

P5-6 cont'd

Task 3. Calculate $\left(-\frac{dP_A}{dZ}\right)$ and plot vs Z to find $\left(-\frac{dP_A}{dZ}\right)$

Plot $\left(-\frac{dP_A}{dZ}\right)$ vs (P_A) on log-log paper to find alpha.

Task 4. Take ratio of initial rates at $P_{A,H_2} = 3.0$ torr and $P_{A,H_2} = 1.5$ torr

$$\frac{\left(-\frac{dP_A}{dZ}\right)_{0.1}}{\left(-\frac{dP_A}{dZ}\right)_{0.1}} = \frac{k P_{A,01} P_{B,01}^\beta}{k P_{A,01} P_{B,01}^\beta} = \left(\frac{P_{B,01}}{P_{B,01}}\right)^\beta$$

$$\frac{90}{46} = \left(\frac{3}{1.5}\right)^\beta \quad \text{Hence } \beta = .97 - 1.0$$

$$\text{Therefore } -r_A = k \left[P_A P_B - \frac{P_C}{K_p} \right]$$

We know $\gamma = 1$ because of thermodynamic consistency. I.e.

$$-r_A = 0 = k \left[P_{A,e} P_{B,e} - \frac{P_{C,e}}{K_p} \right]$$

$$K_p = \frac{P_{C,e}}{P_{A,e} P_{B,e}}$$

Task 5. Evaluate k' and K_p

From A, H_2 of 3.0 torr we see equilibrium is reached at $P_{A,e} = 0.01$

$$P_{C,e} = 0.129 - 0.01 = .119$$

$$P_{B,e} = 3.0 - .119 = 2.881$$

$$K_p = \frac{.119}{(.01)(2.881)} = 4.13 \text{ (torr)}^{-1}$$

From initial rate

$$-\frac{dP_A}{dZ} = 90 \times 10^{-3} \frac{\text{torr}}{\text{cm}} = k' (.129 \text{ torr}) (3.0 \text{ torr})$$

$$k' = 0.23 \text{ (torr cm)}^{-1}$$

P5-7 Given: Data for the decomposition of dimethylether in a gas phase.
constant volume reactor at $T = 504^\circ\text{C} = 777^\circ\text{K}$

Time	0	390	777	1195	3155	-
P	312	408	488	562	799	931



cont'd

$$\lambda_0 = 1, \delta = 3 - 1 = 2 \therefore \varepsilon = 2 \quad V = V_0 \left(\frac{P_0}{P} \right) (1 - \varepsilon X) = V_0 \quad \text{const. vol.}$$

arranging

$$P = P_0 (1 + \varepsilon X) \text{ at } t = \infty, X = X_{Af}$$

$$\frac{-P_0}{\varepsilon P_0} = \frac{911 - 312}{2(312)} = \frac{619}{624} = 1.0 \therefore \text{Assume reaction is irreversible.}$$

$$-\frac{N_{A0}}{V_0} \frac{dX}{dt} = r_A ; \text{Assume: } -r_A = k C_A \text{ (i.e. 1st order)}$$

$$, [1 - X] (V = \text{const.}) \text{ Then: } C_{A0} \frac{dX}{dt} = k C_{A0} (1 - X)$$

$$\frac{P}{P_0} \Rightarrow \frac{dX}{dt} = \frac{1}{\varepsilon P_0} \frac{dP}{dt}$$

$$\frac{dP}{dt} = k \left[1 - \frac{P - P_{A0}}{\varepsilon P_0} \right] = \frac{k}{\varepsilon P_0} ((1 + \varepsilon) P_0 - P)$$

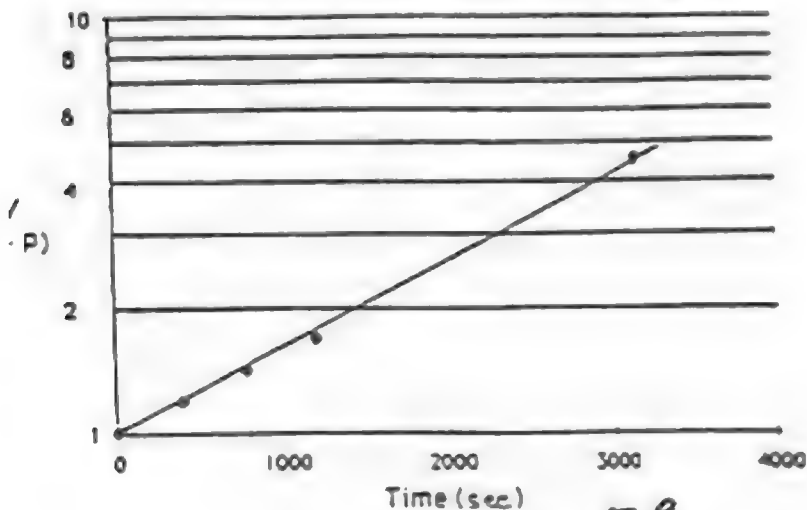
$$\frac{dt}{(1 + \varepsilon) P_0 - P} = \int_0^x k dt, \text{ or } \ln \frac{\varepsilon P_0}{(1 + \varepsilon) P_0 - P} = \ln \frac{2 P_0}{3 P_0 - P} = kt$$

$$\therefore \log \text{ plot of } \frac{2 P_0}{3 P_0 - P} = \frac{624}{936 - P}$$

is linear, reaction is 1st order: it is evident from the plot that

$$k = 0.00048$$

$$\therefore -r_A = 4.8 \times 10^{-4} \text{ sec}^{-1} C_A$$



P5-8

$t(\text{min})$	10	20	30	40	50	60
$C_A(\text{ppm})$	2.45	1.74	1.23	0.88	0.62	0.44

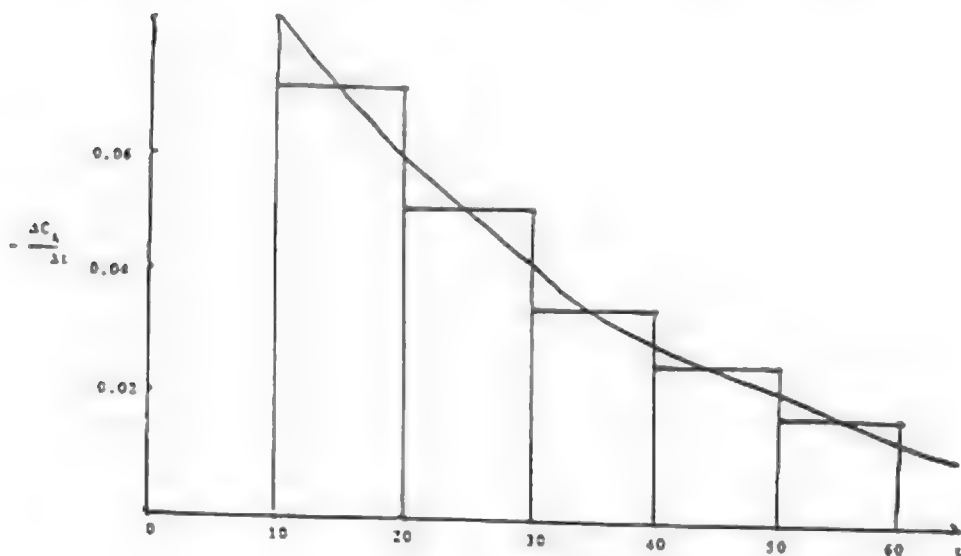
(a) Mole Balance: constant V

$$\frac{dC_A}{dt} = r_A = -k C_A^a$$

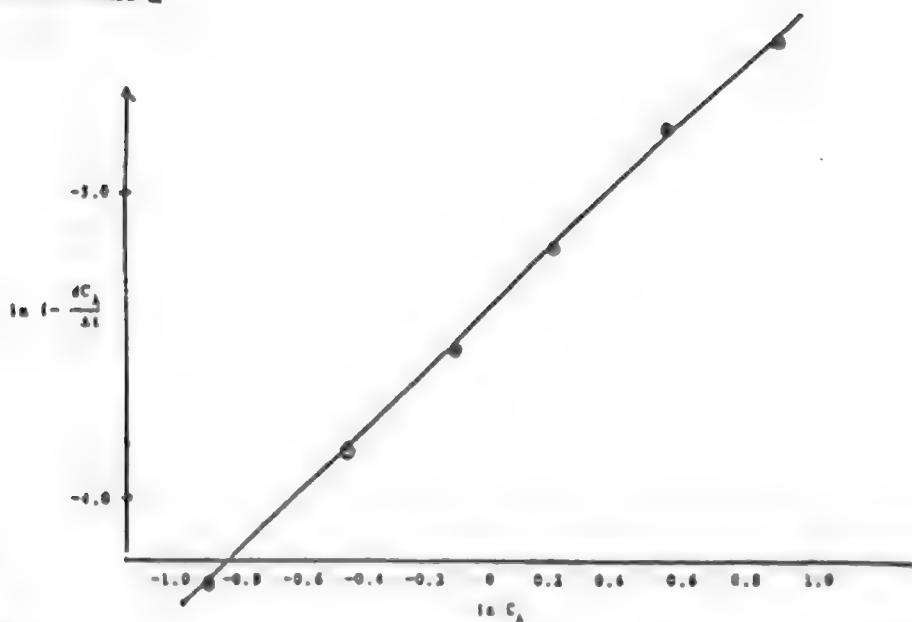
$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + a \ln C_A$$

Differentiation

$t(\text{min})$	10	20	30	40	50	60
$\Delta t(\text{min})$	10	10	10	10	10	
$C_A(\text{ppm})$	2.45	1.74	1.23	0.88	0.62	0.44
$\Delta C_A(\text{ppm})$	-0.71	-0.51	-0.35	-0.26	-0.18	
$\frac{\Delta C_A}{\Delta t} \left(\frac{\text{ppm}}{\text{min}}\right)$	-0.071	-0.051	-0.035	-0.026	-0.018	



P5-8 cont'd



After plotting and differentiating by equal area


$-dC_A/dt$	0.082	0.061	0.042	0.030	0.0215	0.014
$\ln(-dC_A/dt)$	-2.501	-2.797	-3.170	-3.507	-3.840	-4.269
$\ln C_A$	0.896	0.554	0.207	-0.128	-0.478	-0.821

Using linear regression: $\alpha = 1.0$

$$\ln k = -3.3864 \rightarrow k = 0.0344 \text{ min}^{-1}$$

(b)

$$\frac{dC_A}{dt} = v_{rA} = F_B$$

$F_B \rightarrow \boxed{}$


$$r_A = -0.0344 \frac{\text{ppm}}{\text{min}} = -0.0344 \frac{\text{mg}}{\text{l min}} \text{ at } C_A = 1 \text{ ppm}$$

$$F_B = (25000 \text{ gal}) (0.0344 \frac{\text{mg}}{\text{l min}}) \frac{60 \text{ min}}{\text{hr}} \frac{1 \text{ g}}{1000 \text{ mg}} (\frac{3.785 \text{ l}}{453.6 \text{ g}}) \frac{1}{\text{gal}} = 0.429 \frac{\text{lbm}}{\text{hr}}$$

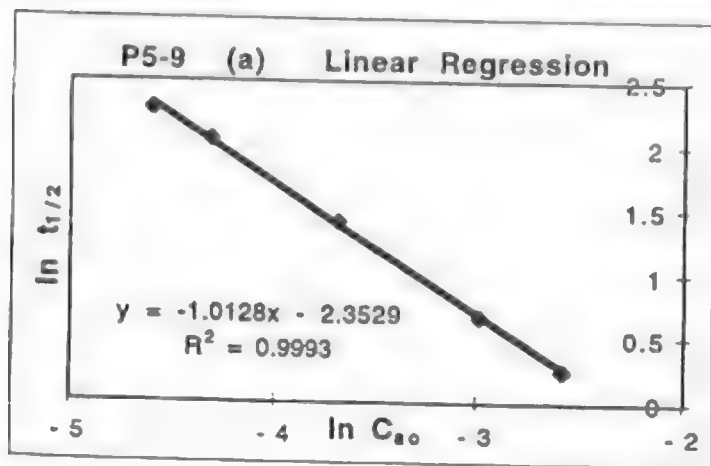
P5-9

(a) Method of Half Lives

Linear Regression:

Run	C_{A0}	$t_{1/2}$	$\ln C_{A0}$	$\ln t_{1/2}$
1	0.025	4.1	-3.689	1.411
2	0.0133	7.7	-4.320	2.041
3	0.01	9.8	-4.605	2.282
4	0.05	1.96	-2.996	0.673
5	0.075	1.3	-2.590	0.262
6	0.025	2		

Plot $\ln C_{A0}$ vs. $\ln t_{1/2}$



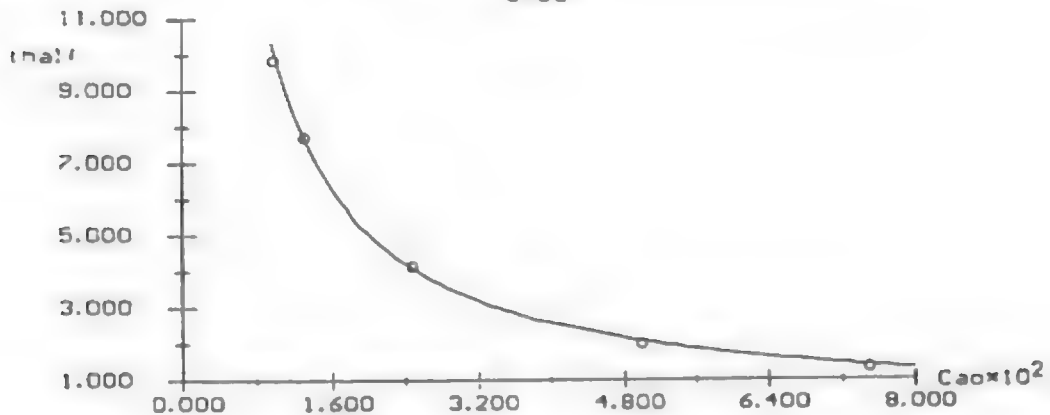
From Linearization:

$$\alpha = 1 - \text{slope} = 2.1029 \approx 2$$

$$k = \frac{(2^{(\alpha-1)} - 1)e^{-\text{intercept}}}{\alpha - 1} = 10.52$$

5-12

5-9a



Model: $t_{half} = (2^{(\alpha-1)} - 1) / (k \alpha (1/C_{A0}^{\alpha-1}))$

$\alpha = 1.97725$

$k = 8.99184$

2 positive residuals, 3 negative residuals. Sum of squares = 0.070594

(b)

Using the equation:

$$k = \frac{(2^{(\alpha-1)} - 1)}{t_{1/2}(\alpha - 1)} \left(\frac{1}{C_{A0}^{\alpha-1}} \right)$$

Solve for k at 110°C.

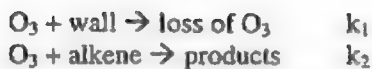
k @ 110°C is 20

k @ 100°C is 10.52

From these values of k we can calculate the activation energy (E).

$$E = \frac{-\ln \frac{k_2}{k_1} R}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = -5876 \text{ J/mol}$$

P5-10



$$-r_{\text{O}_3} = \frac{dC_{\text{O}_3}}{dt} = k_1 + k_2 \frac{C_s}{C_{\text{O}_3}}$$

Using POLYMATH's non-linear regression we can find the values for k_1 and k_2 .

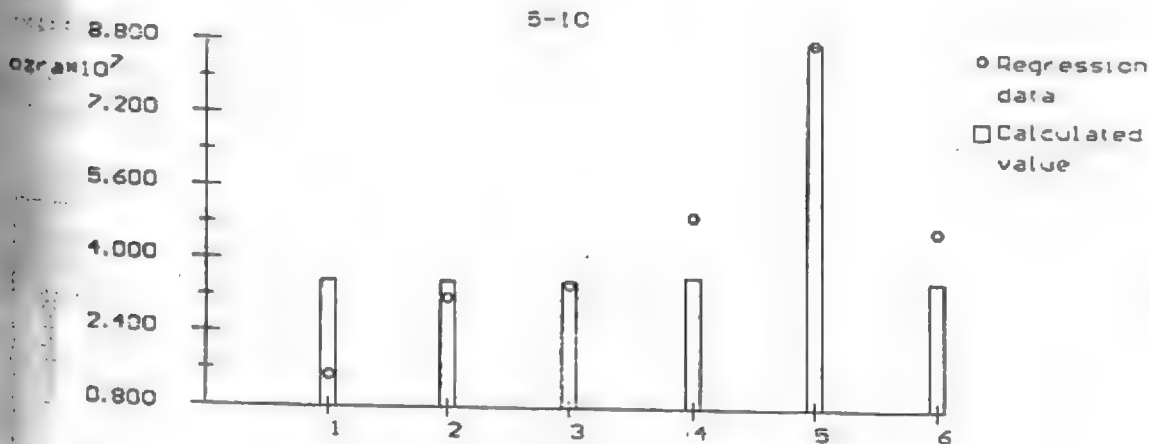
4-10

ozra

Coz

Cbu

	ozra	Coz	Cbu
1	1.5e-07	0.01	1e-12
2	3.2e-07	0.02	1e-11
3	3.5e-07	0.015	1e-10
4	5e-07	0.005	1e-09
5	8.8e-07	0.001	1e-08
6	4.7e-07	0.018	1e-09



Model: $\text{ozra} = k_1 + k_2 \text{Cbu} / \text{Coz}$

$k_1 = 3.54558\text{e-}07$

$k_2 = 0.0528758$

2 positive residuals, 4 negative residuals. Sum of squares = 7.39236e-14

5-14

P5-11 Given: Plot of percent Decomposition of NO_2 vs. V/F_{A0}

$$X = \frac{\% \text{ Decomposition of } \text{NO}_2}{100}$$

Assume that $-r_A = k C_A^2$

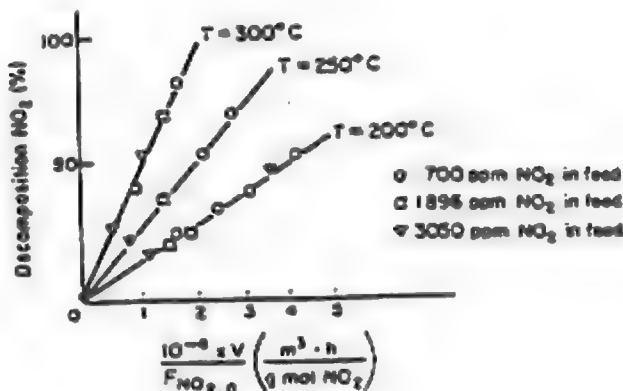
For a CSTR $V = \frac{F_{A0} X}{-r_A}$

or $\frac{V}{F_{A0}} = \frac{X}{-r_A} = \frac{X}{k C_A^n}$

with $n = 0$ $X = k \left(\frac{V}{F_{A0}} \right)$

X is linear with V/F_{A0} , as figure to the right shows

\therefore reaction is zero order. ans.



$$N_S = \text{moles of } \text{SiO}_2 = \frac{A_c \rho_s \delta}{MW_s}$$

A_c = cross sectional area

ρ_s = silicon dioxide density

MW_s = molecular weight of $\text{SiO}_2 = 60.0$

δ = depth of Si

$$N_F = \text{moles of HF} = \frac{w \rho V}{100 MW_F}$$

w = weight percentage HF in solution

ρ = density of solution

V = volume of solution

MW_F = molecular weight of HF 20.0

Assume the rate law is $-r_s = k C_F^a$

5-15

cont'd

Rate balance $\frac{dN_S}{dt} = r_s V$

$$-\frac{A_c \rho_s}{MW_s} \frac{d\delta}{dt} = k \left(\frac{w_0 V}{100 V MW_F} \right)^a V$$

$$-\frac{d\delta}{dt} = \frac{k MW_s}{(100)^a A_c \rho_s} \left(\frac{\rho}{MW_F} \right)^a V w^a$$

$$-\frac{d\delta}{dt} = \beta w^a \text{ where } \beta = \frac{k MW_s}{(100)^a A_c \rho_s} \left(\frac{\rho}{MW_F} \right)^a V$$

$$\ln \left(-\frac{d\delta}{dt} \right) = \ln \beta + a \ln w$$

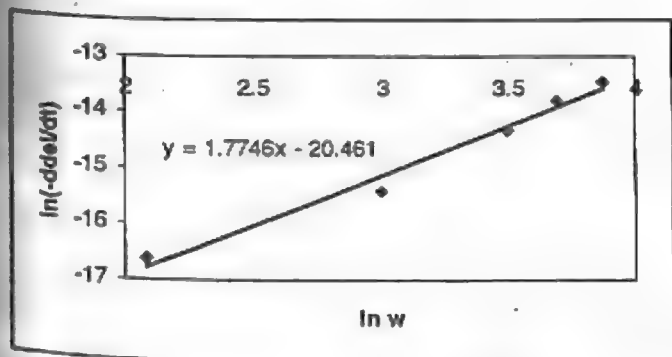
$\ln \left(-\frac{d\delta}{dt} \right)$	-16.629	-15.425	-14.326	-13.816	-13.479
$\ln w$	2.079	2.996	3.497	3.689	3.871

where $\left(-\frac{d\delta}{dt} \right)$ in $\left(\frac{m}{min} \right)$

Linear regression between $\ln \left(-\frac{d\delta}{dt} \right)$ vs. $\ln w$, we have:

slope = $a = 1.775$; intercept = $\ln \beta = -20.461$

or $\beta = 1.2986 \times 10^{-9}$



5-16

P5-12 cont'd

$$\beta = \frac{kMW}{A_c \rho_s} \left(\frac{\rho}{MW_F} \right)^{1.775} V$$

$$A_c = (10 \times 10^{-6} \text{ m})(10 \text{ m})(2 \text{ sides})(1000 \text{ wafers}) = 0.2 \text{ m}^2$$

$$MW_s = 60 \text{ g/gmol}$$

$$\rho_s = 2.32 \frac{\text{g}}{\text{ml}} = 2.32 \times 10^6 \frac{\text{g}}{\text{m}^3}$$

(Handbook of Chemistry and Physics, 57th ed., p. B-155)

$$\rho = 1 \frac{\text{g}}{\text{ml}} = 1 \times 10^6 \frac{\text{g}}{\text{m}^3}$$

$$MW_F = 20 \text{ g/gmol}$$

$$V = 0.5 \text{ dm}^3 = 0.5 \times 10^{-3} \text{ m}^3$$

$$\beta = 1.2986 \times 10^{-9}$$

$$1.2986 \times 10^{-9} = \frac{k \left(60 \frac{\text{g}}{\text{gmol}} \right) \left(\frac{1 \times 10^6 \text{ g/m}^3}{20 \text{ g/gmol}} \right)^{1.775}}{(0.2 \text{ m}^2) (2.3 \times 10^6 \frac{\text{g}}{\text{m}^3}) (100)^{1.775}} \times 0.5 \times 10^{-3} \text{ m}^3$$

$$k = 3.224 \times 10^{-7} \left(\frac{\text{m}^3}{\text{gmol}} \right)^{0.775} \text{ min}^{-1}$$

$$\text{Volume of SiO}_2 \text{ removed} = 2(50 \times 10^{-6})(10 \times 10^{-6})(10)(1000) = 1 \times 10^{-5} \text{ m}^3$$

$$\text{Moles of SiO}_2 \text{ removed} = 1 \times 10^{-5} (2.32 \times 10^6) / 60 = 0.386 \text{ mol}$$

$$\text{Moles of HF used} = 6(0.386) = 2.316 \text{ moles}$$

$$\text{Moles of HF available} = 0.5 \times 10^{-3} / 5 \times 1 \times 10^6 / 20 = 5 \text{ moles}$$

$$\text{Final [HF]} = \frac{5 - 2.316}{5} (0.2) = 0.107 \text{ weight fraction} = 10.7\%$$

$$\text{Initial [HF]} = 0.2 \text{ (given)} = 20\%$$

$$\text{Mole balance for HF: } \frac{dN_F}{dt} = 6 \frac{dN_S}{dt}$$

$$- \frac{\rho_s V}{N_F} \frac{dw}{dt} = 6 k \left(\frac{w \rho}{100 MW_F} \right)^a V \quad \text{where } a = 1.775$$

5-17

PS-12 cont'd

$$-\int_{20}^{10.7} \frac{dw}{w^{1.775}} = 6 k \left(\frac{p}{100HW_F} \right)^{0.775} \int_0^t dt$$

$$\frac{1}{(0.775)} \left(\frac{1}{w^{0.775}} \right) \Big|_{20}^{10.7} = (6) (3.224 \times 10^{-7}) \left(\frac{1 \times 10^6}{20 \times 100} \right)^{0.775} t$$

$$\frac{1}{(0.775)} \left[\frac{1}{(10.7)^{0.775}} - \frac{1}{(20)^{0.775}} \right] = 2.389 \times 10^{-4} t$$

$$t = 330 \text{ min}$$

PS-13

First,

$$r_A = \frac{F_A}{\Delta W}$$

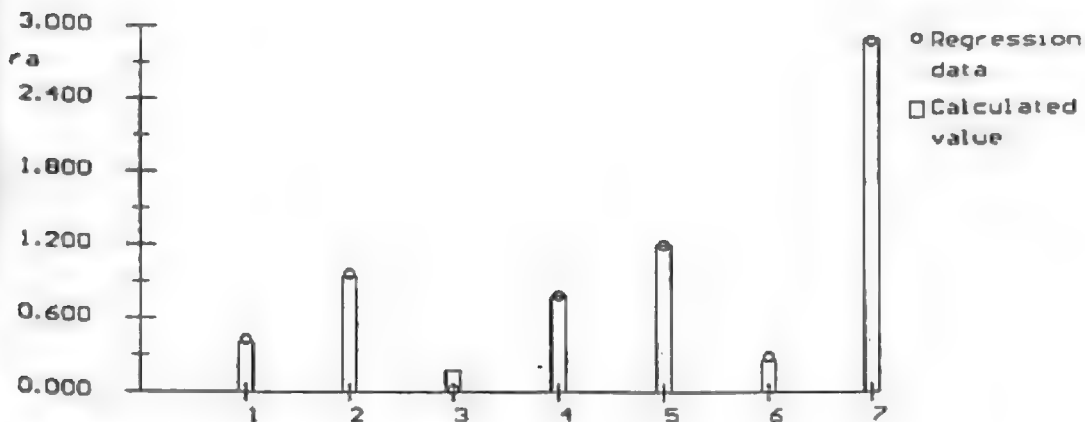
$$\Delta W = 0.5$$

Using POLYMATH's non-linear regression, the following results were found:

$$k = 6.8$$

$$\alpha = 1$$

$$\beta = .2$$



Model: $r_A = k \times P^{\alpha} \times Po^{2\beta}$

$$k = 6.80214$$

$$\beta = 0.201097$$

$$\alpha = 1.03491$$

5 positive residuals, 2 negative residuals. Sum of squares = 0.024629

P5-14

	F_{T0} gmole/hr	P_{A0} atm	P_{B0} atm	θ_B	y_P	X	P_A atm	P_B atm	$-r_A$ gmole/hr-kg
1	1.7	0.5	0.5	1	0.05	0.05	0.475	0.475	1.0625
2	1.2	0.5	0.5	1	0.07	0.07	0.465	0.465	1.0500
3	0.6	0.5	0.5	1	0.16	0.16	0.420	0.420	1.200
4	0.3	0.4	0.6	1.5	0.16	0.2	0.320	0.520	0.600
5	0.75	0.6	0.6	1	0.10	0.10	0.540	0.540	0.9375
6	2.75	0.6	0.4	0.67	0.06	0.05	0.570	0.370	2.0625

$$F_T = F_{T0}$$

$$P_A = C_A RT = C_{A0} RT (1 - X) = P_{A0} (1 - X)$$

$$P_B = C_B RT = C_{A0} RT (\theta_B - X) = P_{A0} (\theta_B - X)$$

$$X = \frac{y_P F_{T0}}{2 F_{A0}} = \frac{y_P}{2 y_{A0}} = \frac{y_P (1 - \theta_B)}{2}$$

$$-r'_A = \frac{1}{2} r'_B = \frac{F_{A0} X}{W} = \frac{F_P}{2W} = \frac{y_P F_{T0}}{2W}$$

$$-r'_A = k P_A^\alpha P_B^\beta$$

$$\ln(-r'_A) = \ln k - \alpha \ln P_A - \beta \ln P_B$$

$$y = A_0 - A_1 X_1 - A_2 X_2$$

P5-14cont'd

Summing over 'n' data points

$$\sum_{i=1}^n y_i = nA_0 + A_1 \sum_{i=1}^n X_{1i} + A_2 \sum_{i=1}^n X_{2i}$$

$$\sum_{i=1}^n X_{1i} y_i = A_0 \sum_{i=1}^n X_{1i} + A_1 \sum_{i=1}^n X_{1i}^2 + A_2 \sum_{i=1}^n X_{1i} X_{2i}$$

$$\sum_{i=1}^n X_{2i} y_i = A_0 \sum_{i=1}^n X_{2i} + A_1 \sum_{i=1}^n X_{1i} X_{2i} + A_2 \sum_{i=1}^n X_{2i}^2$$

Using the data from the following page

$$6 A_0 - 4.695 A_1 - 4.642 A_2 = 0.4403$$

$$A = 0.097$$

$$A_1 = -0.072$$

$$-4.695 A_0 + 3.8837 A_1 + 3.5733 A_2 = -0.026$$

$$A_2 = 0.0935$$

$$A_3 = -0.1974$$

$$-4.695 A_0 + 3.5733 A_1 + 3.6858 A_2 = -0.5866$$

$$A_0 = -0.7423 = \ln k$$

$$\text{ans } || k = 0.476^{\text{atm}} \text{ gmole/hr-kg}$$

$$A_1 = 0.9639 = \alpha - 1.0$$

$$A_2 = -2.035 = \beta - 2.0$$

|| ans

$-r_A'$ gmole/hr-kg	P_A atm	P_B atm	y_i $\ln(-r_A')$	X_{1i} $\ln P_A$	X_{1i}^2 $(\ln P_A)^2$	X_{2i} $\ln P_B$	X_{2i}^2 $(\ln P_B)^2$	$X_{1i} X_{2i}$ $\ln P_A \ln P_B$
1.0625	0.475	0.475	0.0606	-0.7444	0.5542	-0.7444	0.5542	0.5542
1.0500	0.465	0.465	0.0488	-0.7657	0.5863	-0.7657	0.5863	0.5863
1.200	0.420	0.420	0.1823	-0.8673	0.7523	-0.8673	0.7523	0.7523
0.600	0.320	0.320	-0.5108	-1.139	1.298	-0.6339	0.4027	0.7248
0.9375	0.340	0.340	-0.0643	-0.6161	0.3797	-0.6161	0.3797	0.3797
2.0423	0.370	0.370	0.7239	-0.5621	0.3160	-0.9941	0.9885	0.5588
		$\sum_{i=1}^n$	0.4403	-4.695	3.8837	-4.642	3.6858	3.5733

P5-15

$$-r_A = k_0 e^{(-E/RT)} C_A^a$$

$$\text{so } \frac{-r_{A1}}{-r_{A3}} = [\exp \{(-E/R)(1/T_1 - 1/T_3)\}] (C_{A1}/C_{A3})^a$$

$$\ln (-r_{A1}/-r_{A3}) = -E/R (1/T_1 - 1/T_3) + a \ln (C_{A1}/C_{A3})$$

$$\frac{\ln(-r_{A1}/-r_{A3})}{(1/RT_1 - 1/RT_3)} = -E + a \frac{\ln(C_{A1}/C_{A3})}{(1/RT_1 - 1/RT_3)}$$

Run number	1	2	4	5
$\frac{\ln(-r_{A1}/-r_{A3})}{(1/RT_1 - 1/RT_3)}$	-2792.94	-3035.27	-2472.3	-2301.14
$\frac{\ln(C_{A1}/C_{A3})}{(1/RT_1 - 1/RT_3)}$	-739.50	-902.18	-524.47	-409.48

Linear regression yields

$$E = 1690 \text{ atm l/mol}$$

$$a = 1.49$$

Using any data point, we obtain

$$k_0 = 3.16 \times 10^{10} \text{ (mol/l)}^{-0.49}/s$$

P5-16

D)



$$-r_1 = k_A C_A + k_B C_B$$

$$-\frac{dC_1}{dt} = k_A C_{A0}(1 - X_A) + k_B C_{B0}(1 - X_B)$$

$$C_1(t) = C_A(t) + C_B(t) = C_{A0}(1 - X_A) + C_{B0}(1 - X_B)$$

$$C_1(t) = C_{A0}(1 - X_A + \Theta_B - X_B) = C_{A0}(1.75 - X_A - X_B)$$

$$-\frac{dC_1}{dt} = C_{A0}(k_A - k_A X_A + k_B \Theta_B - k_B X_B)$$

$$-\frac{dC_1}{dt} = C_{A0}(k_A - k_A X_A + 0.75k_B \Theta_B - k_B X_B)$$

P4-16 cont'd

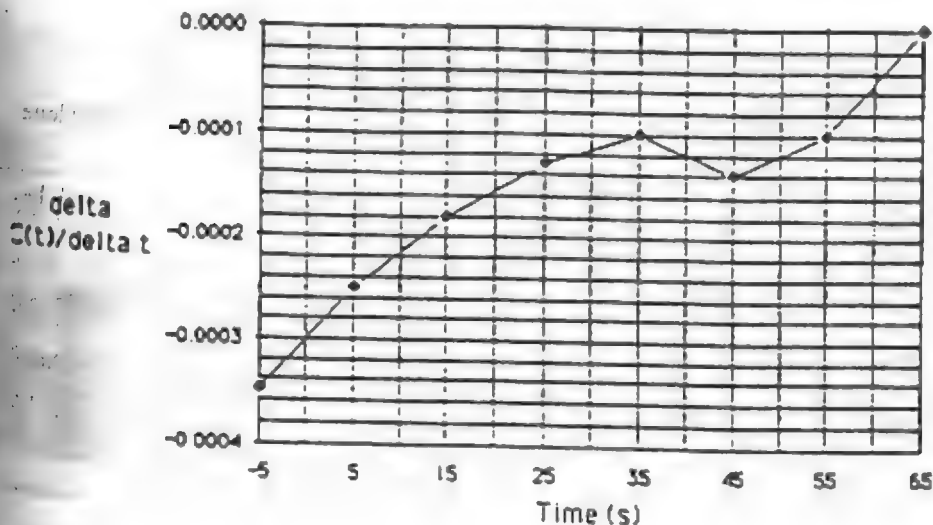
$$\text{II) } D \frac{k_D}{\text{prod}} - \frac{dC_{II}}{dt} = -r_{II} = k_D C_D^2 = k_D C_{D0}^2 (1-X_D)^2$$

$$C_{II}(t) = C_D(t) = C_{D0} (1-X_{D0})$$

so,

t(sec)	0	10	20	30	40	50	60
C(t) kmol/m ³	0.014	0.0115	0.0097	0.0084	0.0074	0.0069	0.0050
If I. $w = X_A + X_B$	0	0.313	0.538	0.700	0.823	1.00	1.123
If II. X_D	0	0.179	0.307	0.400	0.471	0.571	0.643
$\frac{\Delta C(t)}{\Delta t}$	-2.5×10^{-4}	-1.8×10^{-4}	-1.3×10^{-4}	-1×10^{-4}	-1.4×10^{-4}	-1×10^{-4}	
$-\frac{\Delta C(t)}{\Delta t}$	$+2.7 \times 10^{-4}$	$+2.1 \times 10^{-4}$	$+1.6 \times 10^{-4}$	$+1.2 \times 10^{-4}$	$+1.2 \times 10^{-4}$	$+1.2 \times 10^{-4}$	$+0.8 \times 10^{-4}$
If II. $C_{D0}^2 (1-X_D)^2$	1.96×10^{-4}	1.321×10^{-4}	9.413×10^{-5}	7.06×10^{-5}	5.483×10^{-5}	3.61×10^{-5}	2.30×10^{-5}
k_D	1.378	1.663	1.700	1.701	2.188	1.527	1.203

If II were true, all k_D 's should be the same \rightarrow II is not true



P5-17

- (a) Experimental Plan to find the rate law for the hydrogenation of cyclopentane on a $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst:
1. Since this is a stable catalyst we don't have to worry about catalyst decay and an Integral Reactor will be used.
 2. Perform several different runs, holding C_{A0} and W constant while F_{A0} is varied from run to run.
 3. Plot $X_{A,\text{out}}$ vs. W/F_{A0} for all runs.
 4. Fit a curve through all points which passes through the origin. The slope at any point is the reaction rate. Record the slope and corresponding C_{A0} for many different X_A values. These data can be used to determine the rate law.
- (b) Experimental Plan to find the rate law for the liquid-phase production of methyl bromide from an aqueous solution of methyl amine and bromine cyanide:
1. For a liquid-phase reaction without a catalyst, use a batch reactor.
 2. While running the reaction record both C_A and C_B at equal time intervals
 3. Repeat to ensure accurate data.
- (c) Experimental Plan to find the rate law for the acid-catalyzed production of ethylene glycol from an aqueous solution of ethylene oxide:
1. Since this is an aqueous solution with a soluble catalyst, a batch reactor will be used.
 2. Several different runs will be done with different acid concentrations to determine the effect of catalyst concentration on the rate of reaction.
 3. For each run record C_A at equal time intervals. Use this data to determine the effect of C_A on the rate law.

P5-18

a)

Numerical Method

$$\text{Initial Point : } \left(\frac{dC_A}{dt} \right)_{i_0} = \frac{-3 * 2.00 + 4 * 1.31 - 0.95}{2 * 2} = -0.43$$

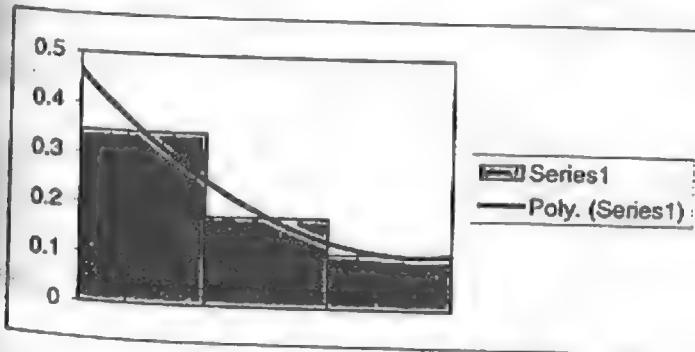
$$\text{Interior Points : } \left(\frac{dC_A}{dt} \right)_{i_1} = \frac{0.95 - 2.00}{2 * 2} = -0.26$$

$$\left(\frac{dC_A}{dt} \right)_{i_2} = \frac{0.73 - 1.31}{4} = -0.15$$

$$\text{Final Point : } \left(\frac{dC_A}{dt} \right)_{i_3} = \frac{1.31 - 4 * 0.95 + 3 * 0.73}{4} = -0.075$$

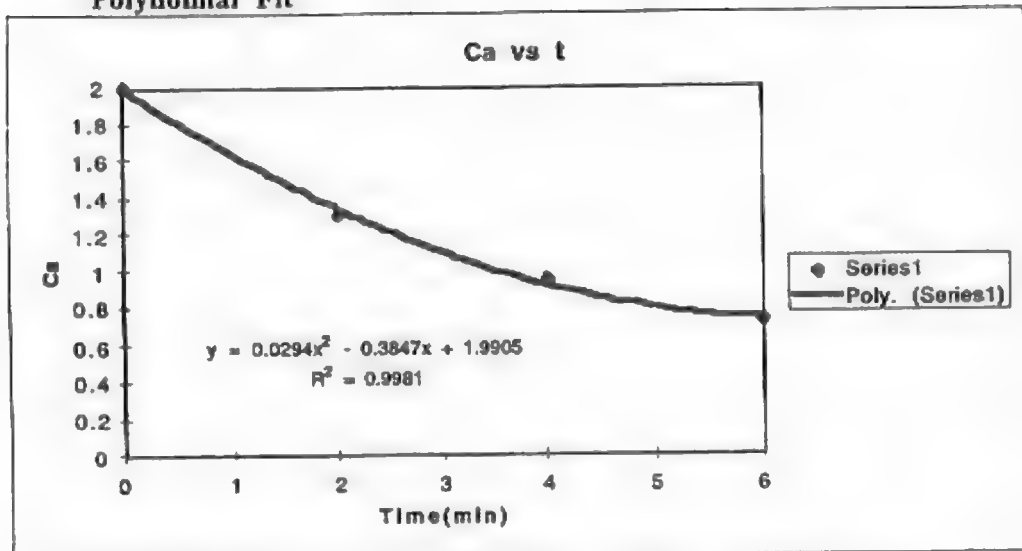
Graphical Method

Ca	Δt	ΔCa	$\Delta Ca / \Delta t$	dCa/dt
0	2			0.46
2	1.31	2	-0.69	-0.345
4	0.95	2	-0.36	-0.18
6	0.73	2	-0.22	-0.11
				0.111



Noticing where the trendline crosses the edges of the bars we will get our values for $-dCa/dt$.

5-18 cont'd
Polynomial Fit

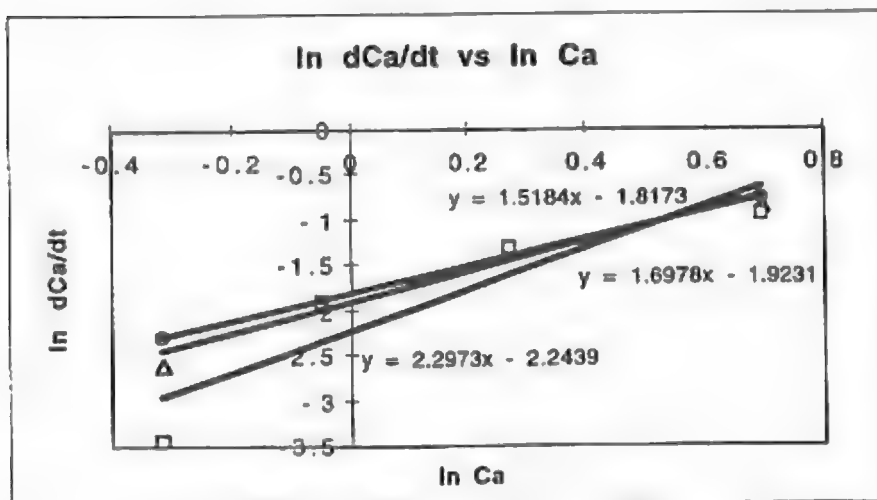


From the graph, we determine the equation for C_A as a function of time:

$$\frac{dC_A}{dt} = 0.0588t - 0.3847$$

Using that we can find and graph the derivative of C_A at any time.
Graphs of the natural log plot of the derivative are given below.

Triangles represent the plot made by the Numerical Technique; circles represent the Graphical Technique; and squares represent polynomial fitting



P5-18 cont'd

- b) Reaction order approximations:
 Numerical Technique - 1.5
 Graphical Technique - 1.5
 Polynomial Technique - 2

c)

$$\frac{dC_A}{dt} = r_A$$

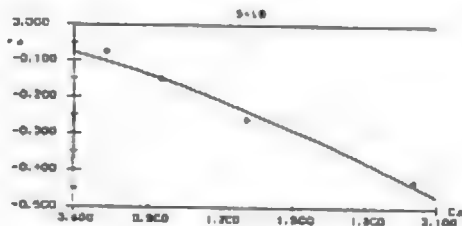
$$-r_A = kC_A^\alpha$$

Combine and then integrate from $(0, C_{A0})$ to (t, C_A) to get

$$C_A = [C_{A0}^{1-\alpha} - (1-\alpha)kt]^{1/(1-\alpha)}$$

Plug that into POLYMATH's non-linear regression and find that $\alpha = 1.5$ and $k = .16$

	r_A	C_A
1	-0.43	2
2	-0.26	1.31
3	-0.15	0.95
4	-0.075	0.73



Model: $-r_A = kC_A^\alpha$
 $k = 0.159354$
 $\alpha = 1.4575$
 2 positive residuals, 2 negative residuals. Sum of squares = 0.00129113

Matrix of correlation coefficients for the nonlinear correlation equation

	k	α
k	1	-0.871145
α	-0.871145	1

Param.	Converged Value	0.95 conf. interval	lower limit	upper limit
k	0.159354	0.0671333	0.0922212	0.225488
α	1.4575	0.714352	0.743149	2.17185

Model: $-r_A = kC_A^\alpha$

$k = 0.159354$

$\alpha = 1.4575$

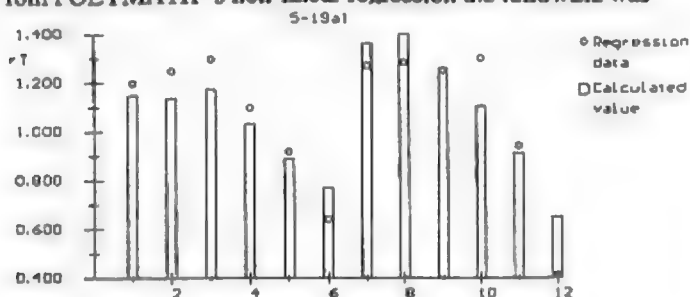
2 positive residuals, 2 negative residuals. Sum of squares = 0.00129113

- d) No answer will be given.

P5-19

a) 1)
obtained

From POLYMATH's non-linear regression the following was



Model: $rT = k \cdot Pn^{\alpha} / (1 + Pn^2)^{\beta}$

$k = 1.14015$

$\beta = -0.0300691$

$\alpha = 0.184305$

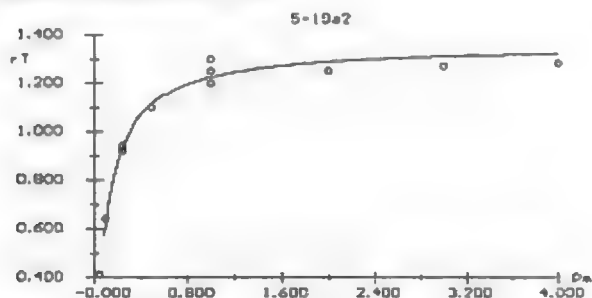
7 positive residuals, 5 negative residuals. Sum of squares = 0.200197

$k = 1.15$

$\alpha = .18$

$\beta = -.031$

2) Again POLYMATH is used



Model: $rT = k \cdot Pn / (1 + K_M \cdot Pn)$

$k = 12.2562$

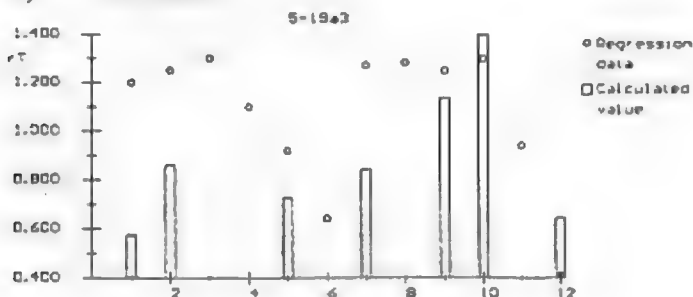
$K_M = 9.02516$

3 positive residuals, 9 negative residuals. Sum of squares = 0.0186383

$k = 12.3$

$K_M = 9.0$

3) POLYMATH



Model: $rT = k \cdot Pn^2 / (1 + K_M \cdot Pn)^2$

$k = 8.40943$

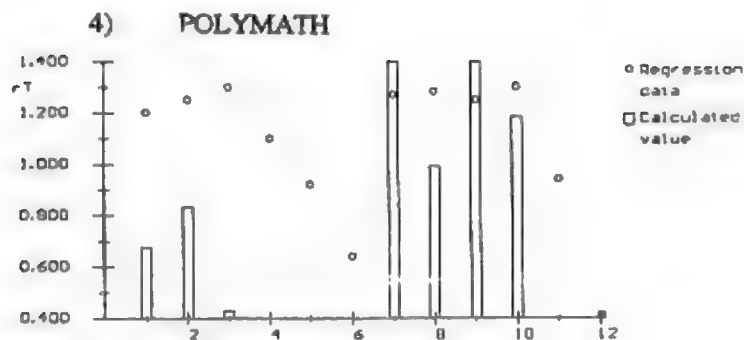
$K_M = 2.8307$

10 positive residuals, 2 negative residuals. Sum of squares = 5.00106

5-27

$$k = 8.4$$

$$K_M = 2.8$$



Model: $rT = k \cdot P_{mPh2} / (1 + K_{mPh2} + K_{H2} \cdot P_{mPh2})$

$$k = 3.26685e+18$$

$$K_{H2} = -2.06168e+18$$

$$K_M = 2.77855e+18$$

10 positive residuals, 2 negative residuals. Sum of squares = 3.89059

$$k = 3.26 \cdot 10^{18}$$

$$K_{H2} = 2.06 \cdot 10^{18}$$

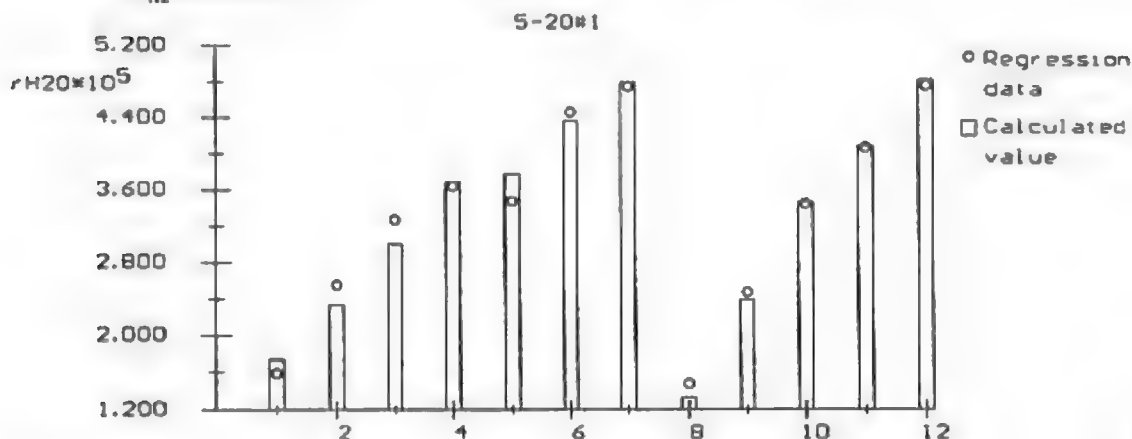
$$K_M = 2.78 \cdot 10^{18}$$

- b) From the above POLYMATH regressions we can see that the best rate law is number two. This is evident because it has the lowest sum of squares.

- c) No answer will be given.

P5-20

Using POLYMATH's non-linear regression, the data was fit to the following parameters. For the first equation: $k = 0.0024$ $K_{NO} = 8.31 \times 10^{15}$
 $K_{H_2} = 1.24 \times 10^{16}$



Model: $rH_2O = k \cdot K_{NO} \cdot P_{NO} \cdot P_{H_2} / (1 + K_{NO} \cdot P_{NO} + K_{H_2} \cdot P_{H_2})$

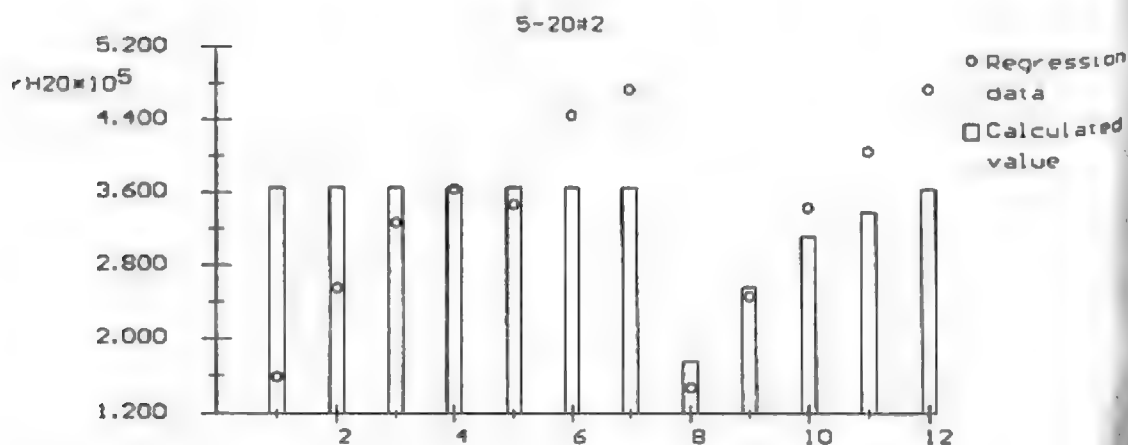
$k = 0.0024218$

$K_{H_2} = 1.24056e+16$

$K_{NO} = 8.31397e+15$

5 positive residuals, 7 negative residuals. Sum of squares = $2.71177e-11$

For the second equation: $k = 0.32$ $K_{NO} = 61.8$ $K_{H_2} = 0.00015$



Model: $rH_2O = k \cdot K_{H_2} \cdot K_{NO} \cdot P_{NO} / (1 + K_{NO} \cdot P_{NO} + K_{H_2} \cdot P_{H_2})$

$k = 0.320466$

$K_{NO} = 61.846$

$K_{H_2} = 0.00015082$

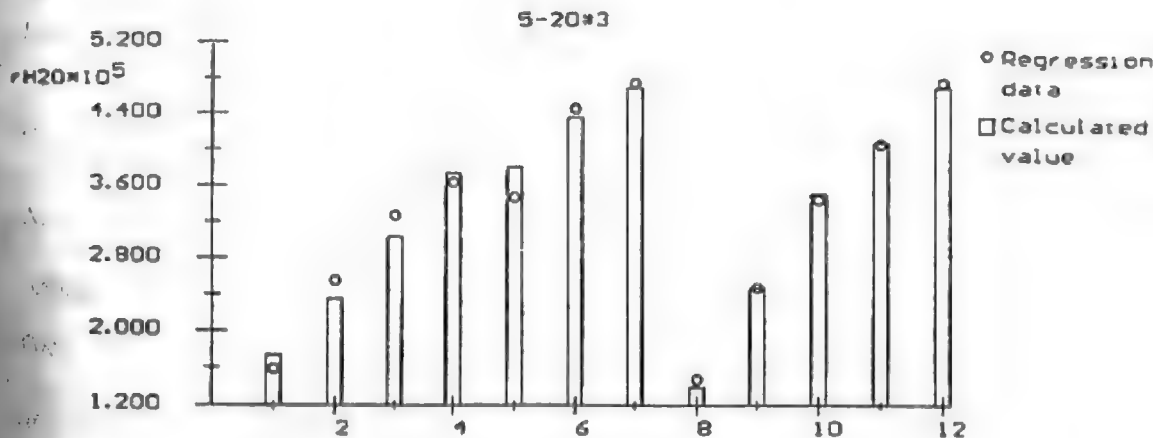
5 positive residuals, 7 negative residuals. Sum of squares = $9.32207e-10$

5-29

PS-20 cont'd

For the third equation:

$$k = 0.00052 \quad K_{NO} = 13.2 \quad K_{H_2} = 18.5$$



Model: $r_{H_2O} = k \times K_{H_2} \times K_{NO} \times P_{NO} \times P_{H_2} / (1 + K_{NO} \times P_{NO} + K_{H_2} \times P_{H_2})^2$

$k = 0.000518948$

$K_{NO} = 13.1894$

$K_{H_2} = 18.5102$

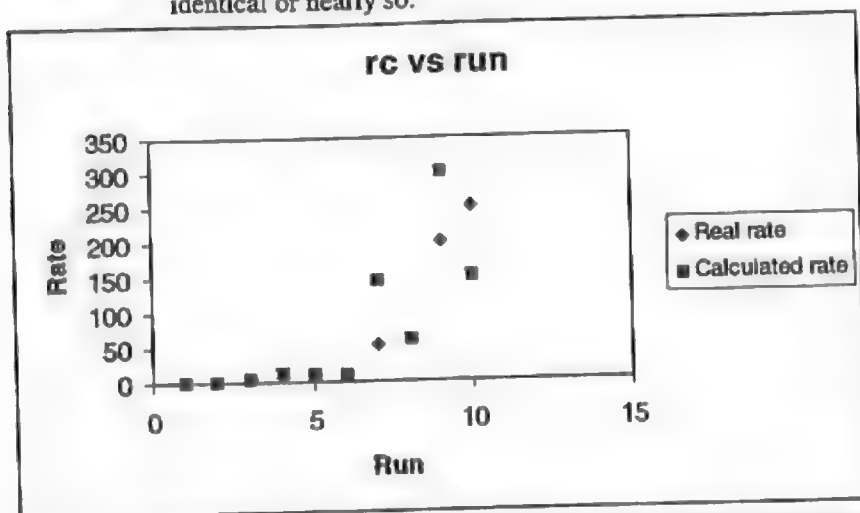
6 positive residuals, 6 negative residuals. Sum of squares = 2.60646e-11

$$r_{H_2O} = \frac{k K_{H_2} K_{NO} P_{NO} P_{H_2}}{(1 + K_{NO} P_{NO} + K_{H_2} P_{H_2})^2}$$

This is the best equation. In the second equation, the calculated value does not change with a change in Hydrogen pressure so it is not a reliable source. The first equation is somewhat reliable, but the values for the Ks are very high and do not make a good answer.

P5-21

- a) This reaction is not elementary, if it were these two graphs would be identical or nearly so:



To obtain the calculated rate, find k from one of the runs and use that one throughout. The graph is similar in the smaller pressures, but as the pressure of A increases the rates differ greatly.

- b) The sequence is specified this way so that r_c is always increasing.
c) No solution will be given.

CDP5-A

Given the reaction $P + \text{NH}_2\text{OH} \rightarrow \text{NH}_2\text{OHP}$

where P is Penicillin and NH_2OHP is hydroxylamine acid (denoted by subscript HA)

Let A = Absorbency, then $C_{\text{HA}} = KA$ where K is some constant.

$$C_p = C_{p0}(1 - X) \quad (\varepsilon = 0 \text{ for liquid phase reaction.})$$

$$C_{\text{HA}} = C_{p0}X = KA \quad \therefore X = \frac{KA}{C_{p0}} \quad \text{when } X = 1 \text{ and } A = A_{\infty}$$

$$\text{At } t = \infty, A_{\infty} = \frac{C_{p0}}{K} \quad \therefore X = \frac{A}{A_{\infty}}$$

Assume reaction is irreversible: $-r_p = kC_p^n = kC_{p0}^n(1 - X)^n$

For a batch, constant volume reactor: $\frac{1}{V} \frac{dN_p}{dt} = \frac{dC_p}{dt} = r_p$

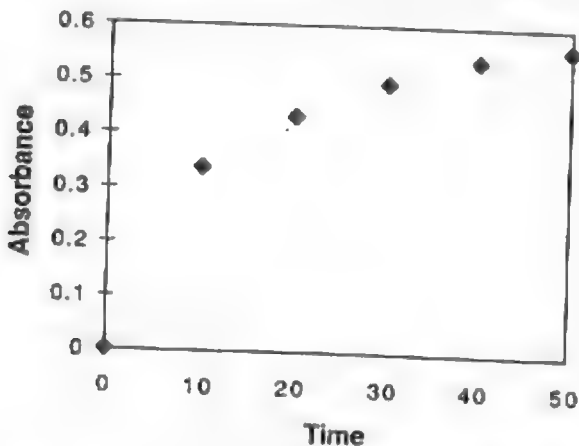
$$\text{or } \frac{dC_p}{dt} = C_{p0} \frac{dX}{dt} = -\frac{C_{p0}}{A_{\infty}} \frac{dA}{dt} = -kC_{p0}^n(1 - X)^n = -kC_{p0}^n(1 - A/A_{\infty})^n$$

$$\text{or } \frac{dA}{dt} = k \left(\frac{C_{p0}}{A_{\infty}} \right)^{n-1} (A_{\infty} - A)^n = K(A_{\infty} - A)^n, \quad \text{where } K = k \left(\frac{C_{p0}}{A_{\infty}} \right)^{n-1}$$

Try integral analysis first. Assume that reaction is zero order:

Then $\frac{dA}{dt} = K$ or $\int_0^A dA = A = Kt$ a plot of A vs. t should be linear if

reaction is zero order. From the plot below, it is evident that the reaction is not zero order:



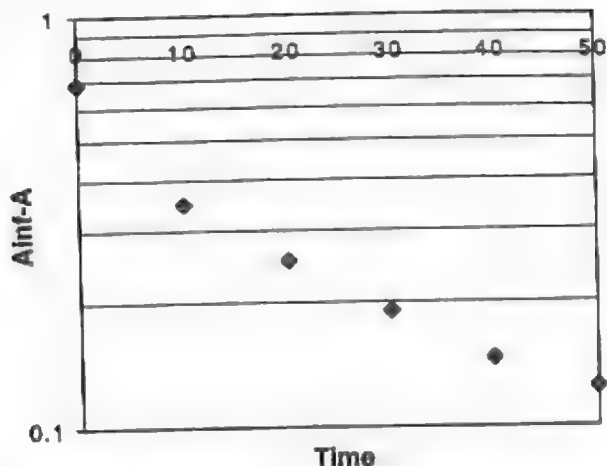
Next, assume that the reaction is first order:

$$\frac{dA}{dt} = K(A_{\infty} - A) \quad \text{or} \quad \int_0^A \frac{dA}{(A_{\infty} - A)} = \int_0^t K dt = \ln \frac{(A_{\infty} - A)}{A_{\infty}} = -Kt$$

\therefore A plot of $(A_{\infty} - A)$ vs. t on semi-log paper should be linear.

CDP5-A (cont'd)

Time	A	$A_{\infty} - A$
0	0	0.685
10	0.337	0.348
20	0.433	0.252
30	0.495	0.190
40	0.539	0.146
50	0.561	0.124
∞	0.685	0

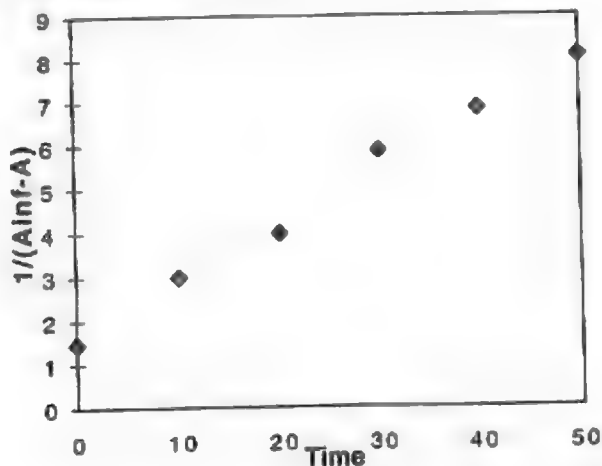


It is evident from the plot that the reaction is not first order. Try second order:

$$\frac{dA}{dt} = K(A_{\infty} - A)^2 \quad \therefore \int_0^A \frac{dA}{(A_{\infty} - A)^2} = \frac{1}{(A_{\infty} - A)} - \frac{1}{A_{\infty}} = Kt$$

$$\text{or } \frac{1}{(A_{\infty} - A)} = \frac{1}{A_{\infty}} + Kt \quad \therefore \text{A plot of } \frac{1}{(A_{\infty} - A)} \text{ vs. } t \text{ should be linear}$$

Time	A	$A_{\infty} - A$
0	0	1.460
10	0.337	2.967
20	0.433	3.968
30	0.495	5.882
40	0.539	6.849
50	0.561	8.065



From the plot, it is evident that a linear relationship exists between $(1/A_{\infty} - A)$ and time; therefore the reaction is second order.

CDP5-B

The rate law for this reaction will be of the form:

$$-r_A = kC_A^n$$

Where n = the order of the reaction and k = the specific reaction rate constant. These are the two parameters we need to find using the data given.

First, we need to plot $\ln(-dC_A/dt)$ vs. $\ln(C_A)$. To do this, we need to know how fast the solution is traveling and at what time the solution reaches an electrode position.

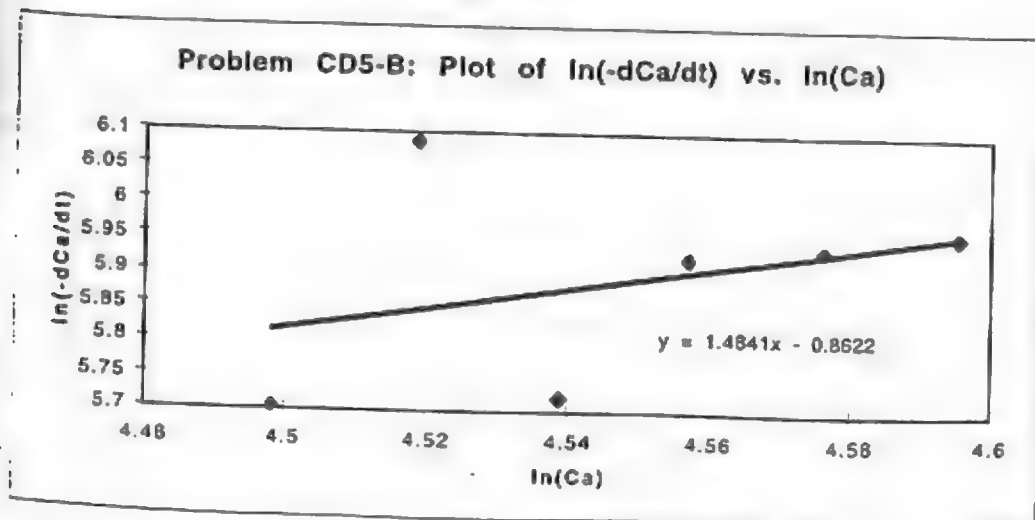
Since the tube diameter is 0.158 cm, the tube cross-sectional area is 0.0196 cm². This allows us to divide the solution volumetric flow rate by the cross sectional area and attain the velocity at which the solution is traveling:

$$\text{Solution velocity} = (19.6 \text{ cm}^3/\text{s}) / (0.0196 \text{ cm}^2) = 1000 \text{ cm/s}$$

Now, if we consider the percent decomposition of HbO₂ as the conversion of the reaction, the percent of HbO₂ still remaining can be our C_A , since we do not know the initial concentration or molar flow rate of HbO₂ in solution.

Electrode Position	1	2	3	4	5	6	7
Time (s)	0	.005	.010	.015	.020	.025	.030
dt (s)	.005	.005	.005	.005	.005	.005	.005
% Decomposition HbO ₂	0	1.93	3.82	5.68	7.2	9.4	10.9
% HbO ₂ left (C_A)	100	98.07	96.18	94.32	92.8	90.6	89.1
dC_A	-	-1.93	-1.89	-1.86	-1.52	-2.2	-1.5
$-dC_A/dt$	-	386	378	372	304	440	300
Average C_A	-	99.035	97.125	95.25	93.56	91.7	89.85

A plot of $\ln(-dC_A/dt)$ vs. $\ln(C_A)$ is then produced:



5-34

CDP5-B cont'd

As can be seen from this plot, the data points are not exactly linear. However, to use the method of differential analysis of rate data, we must find a best-fit line for the data. That best-fit line is drawn in the plot, and the slope is 1.4841. This slope corresponds to the order of the rate law (n). Therefore, the rate law is now:

$$-r_A = kC_A^{1.5}$$

To calculate k, the specific reaction rate constant, we must evaluate the following equation, using the data gathered between electrode points 1 and 2:

$$k = \frac{\left. \frac{dC_A}{dt} \right|_P}{C_A^{1.5} \big|_P} = \frac{386 \cdot \% / s}{99.035^{1.5} \%^{1.5}} 0.39166 s^{-1} \%^{-0.5}$$

Therefore, the specific reaction rate is $0.39166 s^{-1} \%^{-0.5}$, and the final reaction rate law is:

$$-r_A = 0.39166 C_A^{1.5} \% / s$$

CDP5-C

Given: moles of ammonia formed at specific time

Find dC/dt also known as the rate of formation of ammonia

Use the graphical method and the following table is a summary of the results

First use a temperature of 351K

CDP5-C @ 351K					
t	C _N	Δt	ΔC _N	ΔC _N /Δt	dC _N /dt
0	0	0			
			5	0.15	0.03
5	0.15		5	0.125	0.025
					0.027
10	0.275		10	0.21	0.021
					0.023
20	0.485		10	0.165	0.0165
					0.019
30	0.65		10	0.12	0.012
					0.015
40	0.77		10	0.1	0.01
					0.013
50	0.87		10	0.08	0.008
					0.01
60	0.95		10	0.08	0.008
			20	0.13	0.0065
80	1.08				0.008
			20	0.09	0.0045
100	1.17				0.0074
			50	0.145	0.0029
150	1.315				0.007

∴ following way

Next, find the concentrations of GN and N₂H₄. Do this the following way

$$C_{NH_3} = \frac{N_{NH_3}}{V}$$

$$X = \frac{C_{NH_3}}{3 * C_{GN0}}$$

$$C_{GN} = C_{GN0} * (1 - X)$$

$$C_{N_2H_4} = C_{GN0} * (\theta_B - 3 * X)$$

$$.5M + 2.575M = 3.075M$$

$$y_{GN} = \frac{.5}{3.075} = .16$$

$$y_{N_2H_4} = \frac{2.575}{3.075} = .84$$

$$\theta_B = \frac{.84}{.16} = 5.23$$

Once that is done plug into POLYMATH's non-linear regression program with the following table.

5-30351

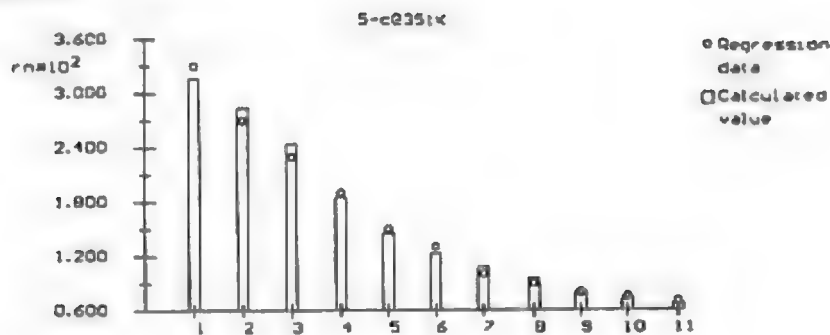
rn

X

Cgn

Ch

#	rn	X	Cgn	Ch
1	0.033	0	0.5	2.575
2	0.027	0.1	0.45	2.47
3	0.023	0.18	0.41	2.35
4	0.019	0.32	0.34	2.14
5	0.015	0.43	0.285	1.97
6	0.013	0.51	0.245	1.85
7	0.01	0.58	0.21	1.75
8	0.009	0.63	0.185	1.67
9	0.008	0.72	0.14	1.54
10	0.0074	0.78	0.11	1.45
11	0.007	0.88	0.06	1.3



Model: $r = k + C_0 \alpha \ln \beta C_0 \ln \beta$

$k = 0.00035948$

$\beta = 4.25705$

$\alpha = -0.611973$

6 positive residuals, 5 negative residuals. Sum of squares = $7.38112e-06$

5-c2351x

Matrix of correlation coefficients for the nonlinear correlation equation

	k	alp	bet
k	1	0.993351	-0.99832
alp	0.993351	1	-0.986061
bet	-0.99832	-0.986061	1

Param.	Converged Value	0.95 conf. interval	lower limit	upper limit
k	0.00035948	0.000628826	-0.000269345	0.000988306
alp	-0.611973	0.574513	-1.21949	-0.0704596
bet	4.25705	1.44831	2.80774	5.70636

Model: $r = k + C_0 \alpha \ln \beta C_0 \ln \beta$

$k = 0.00035948$

$\beta = 4.25705$

$\alpha = -0.611973$

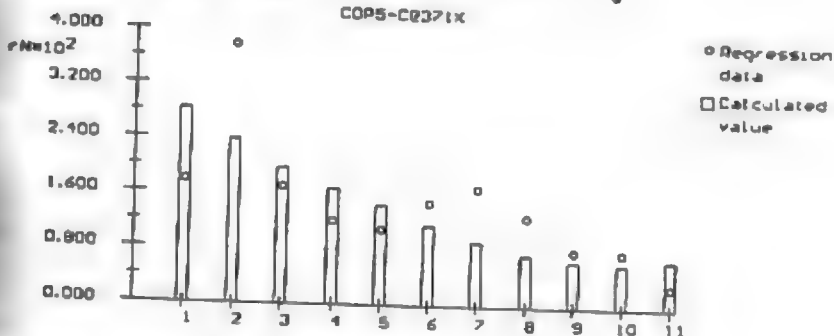
6 positive residuals, 5 negative residuals. Sum of squares = $7.38112e-06$

The answer we get is that $k = 0.00036$
 $\alpha = -2/3$
 $\beta = 4.25$

For the higher temperature, we know alpha and beta so we will just solve for k.
 Create this chart to find dC/dt .

CPS-C @ 371

t	Cn	Δt	ΔCn	$\Delta Cn/t$	$\Delta Cn/t^2$
0	0	0			0.017581
5	0.19		5	0.19	0.038
10	0.345		5	0.155	0.031
20	0.475		10	0.13	0.013
30	0.58		10	0.105	0.0105
40	0.755		10	0.175	0.0175
50	0.865		10	0.13	0.013
60	1.065		10	0.18	0.018
80	1.185		20	0.12	0.008
100	1.32		20	0.135	0.0065
150	1.305		50	0.075	0.0015
					0

Model: $rN = k \cdot Cn^{(-.66)} \cdot CH^{(4.25)}$ $k = 0.000323653$

6 positive residuals, 5 negative residuals. Sum of squares = 0.00046934

CPS-C@371K

Matrix of correlation coefficients for the nonlinear correlation equation

k
1

Param.	Converged value	0.95 conf. interval	lower limit	upper limit
k	0.000323653	9.35865e-05	0.000228067	0.00041924

Model: $rN = k \cdot Cn^{(-.66)} \cdot CH^{(4.25)}$ $k = 0.000323653$

6 positive residuals, 5 negative residuals. Sum of squares = 0.00046934

CDP5-C cont'd

$$\text{So } k = .00032$$

$$\log\left(\frac{0.00036}{0.00032}\right) = \frac{-E}{2.3 \cdot 8.314} \left(\frac{1}{371} - \frac{1}{351} \right)$$

$$E = 6368 \text{ J}$$

CDP5-D

Since oxygen is found in excess, we assume that $-r_{\text{NO}}$ is dependent only on C_{NO} . This gives us a rate law of the form:

$$-r_{\text{NO}} = kC_{\text{NO}}^{\alpha}$$

From the units of the specific reaction rate, we assume that $\alpha = 3$. Now, using equation (5-18) from chapter 5, we can solve for the desired half-lives.

$$t_{1/2} = \frac{2^{\alpha-1} - 1}{k(\alpha-1)} \left(\frac{1}{C_{\text{NO}_0}^{\alpha-1}} \right) = \frac{2^{3-1} - 1}{k(3-1)} \left(\frac{1}{C_{\text{NO}_0}^{3-1}} \right) = \frac{2^2 - 1}{2k} \left(\frac{1}{C_{\text{NO}_0}^2} \right)$$

(a) For $C_{\text{NO}_0} = 3000 \text{ ppm}$:

$$t_{1/2} = \frac{3}{2(1.4 \times 10^{-9} \text{ ppm}^{-2}/\text{min})} \left(\frac{1}{(3000 \text{ ppm})^2} \right) = 119.05 \text{ min}$$

(b) For $C_{\text{NO}_0} = 1 \text{ ppm}$:

$$t_{1/2} = \frac{3}{2(1.4 \times 10^{-9} \text{ ppm}^{-2}/\text{min})} \left(\frac{1}{(1 \text{ ppm})^2} \right) = 1.071 \times 10^9 \text{ min}$$

CDP5-E

Given the data, postulate a rate law.

$$-r_A = kC_A^{\alpha}$$

Then write the design equation in terms of the data given, in this case volume and time.

$$C_A = N_A/V$$

$$N_A = N_{A0}(1-X)$$

$$V = V_0(1+\epsilon X)$$

$$X = \frac{V - V_0}{V_0 \epsilon}$$

$$C_A = \frac{1 - \frac{V - V_0}{V_0 \epsilon}}{V}$$

5-39

CDP5-E **cont'd**

Plug that into the design equation:

$$-\frac{dC_A}{dt} = kC_A^\alpha$$

$$-\frac{d\left(\frac{1 - \frac{V - V_0}{V_0\epsilon}}{V}\right)}{dt} = k' \left(\frac{1 - \frac{V - V_0}{V_0\epsilon}}{V}\right)^\alpha$$

$$k' = k(N_{A0}^{\alpha-1})$$

$$\ln - \frac{d\left(\frac{1 - \frac{V - V_0}{V_0\epsilon}}{V}\right)}{dt} = \alpha \ln \left(\frac{1 - \frac{V - V_0}{V_0\epsilon}}{V}\right) + \ln k'$$

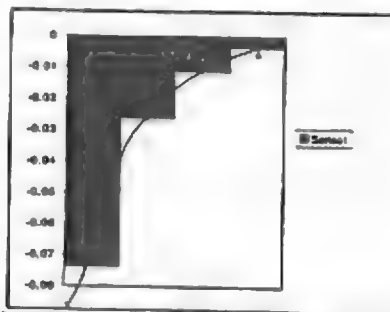
$$k' = \frac{-\frac{d\left(\frac{1 - \frac{V - V_0}{V_0\epsilon}}{V}\right)}{dt}}{\left(\frac{1 - \frac{V - V_0}{V_0\epsilon}}{V}\right)^\alpha}$$

Now find the derivative. To do that use the graphical method.

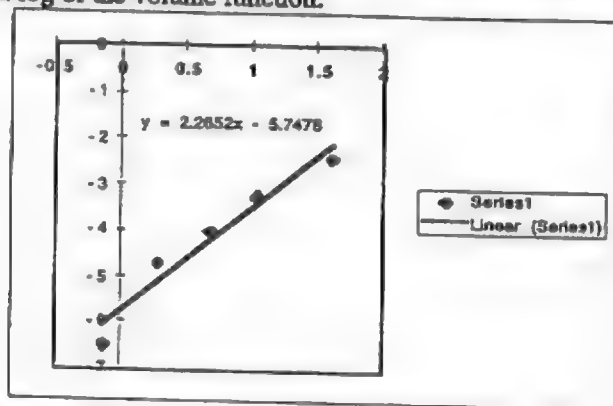
t	$(1 - (V - V_0)/V_0\epsilon)/V$	Δt	$\Delta 1 - (V - V_0)/V_0\epsilon)/V$	$\Delta 1 - (V - V_0)/V_0\epsilon)/V / \Delta t$	$d 1 - (V - V_0)/V_0\epsilon)/V / dt$
0	5	30	-2.211	-0.0737	-0.09
30	2.789	30	-0.785	-0.0262	-0.04
60	2.003	60	-0.679	-0.011	-0.018
120	1.32	120	-0.448	-0.004	-0.009
240	0.88				-0.0015

5-40

The following graph is made.



Once that is done it is the natural log of those values is ready to be graphed. The following graph is the natural log of the derivative of the volume function against the natural log of the volume function.



From the graph we see that α is 2. We can also find k :

$$k' = \frac{.09}{5} = .018$$

$$N_{A0} = y_{A0} N_{T0} = .85 * \frac{303.39 * .2}{8.314 * 313} = .020 \text{ moles}$$

$$k = \frac{k'}{N_{A0}^{\alpha-1}} = \frac{.018}{.02^1} = .9$$

The following rate law is found:

$$-r_A = .9 * C_A^2$$

Now, to determine the volume of the CSTR we must use the design equation and stoichiometry:

$$V = \frac{F_{A0} X}{-r_A}$$

$$C_A = C_{A0} (1 - X)$$

$$C_{A0} = \frac{P_{A0}}{RT_0}$$

$$P_{A0} = y_{A0} P_0 = .6 * 1013.25 \text{ kPa} = 607.95$$

Combining these with the rate law just determined, the following volume is found.

$$V = \frac{F_{A0} X}{.9 * \left(\frac{P_{A0}}{RT} (1 - X) \right)^2} = \frac{16.67 * .8}{.9 * \left[\frac{607.95}{8.314 * 313} (1 - .8) \right]^2} = 6787 \text{ dm}^3$$

5-41

Chapter 6

- P6-1.** An open-ended problem that requires students to create and original problem and solution.
- P6-2.** "What if. . ." problem. Parts (c), (d) and (e) can be used in conjunction with Living Example Problems E6-6 and E6-8.
- P6-3.** This problem concerns thermodynamic equilibrium and multiple reactions. It is usually assigned at the graduate level. The heat of isomerization must be calculated at temperature below 100°C where no other reactions are dominate alternate to P6-5.
- P6-4.** Straight forward problem to reinforce principles of how to choose reactor schemes to maximize the instantaneous selectivity S_{DU} for parallel reactions.
- P6-5.** Thermodynamics and multiple reactions. Alternative to P6-3.
- P6-6.** Maximize S_{DU} for parallel reactions. Parts (c) and (d) allow the student to explore the problem by varying the temperature and pressure.
- P6-7.** This problem concerning drinking and driving has always been a favorite with the students. It is quite straight forward.
- P6-8.** This problem is a new problem on drug medication which has been assigned for the past two years, is similar to P6-7. But it is a little more open-ended than P6-7 in that the student must decide on the amount (one dose or two) of drugs and the times to administer them.
- P6-9.** Maximizing S_{DU} and \$ for series reaction. Parts (a), (b), and (c) are straight forward, and could be one problem by themselves. Parts (c) through (f) allow the student to explore the problem and learn the trends as each reaction is allowed to be reversible. Part (g) involves a packed bed reactor with pressure drop. If all parts are assigned, it would be a fairly long assignment. Good though!!!! (Moose dung pie joke).
- P6-10.** Straight forward problem that is fairly short. Points out that the CSTR temperature can be adjusted to maximize overall selectivity.
- P6-11.** This problem is a medium-length (Ca.40 minutes) straight forward problem it reinforces relating relative rates of reaction. It is most always assigned as an "in class" problem.
- P6-12.** Fairly straight forward problem using POLYMATH. Allows for temperature variation to find optimum operating conditions.

- P6-13. This problem is usually assigned as it is straight forward and encompasses all the facets of liquid phase reactor design for multiple reactions.
- P6-14. This problem is a more complicated, alternative to P6-12. Parts (a) through (d) are reasonably straight forward.
- P6-15. Extends the **Living Example Problem E6-6**, to include a 3rd reaction. Allows for parameter variation, and because E6-6 can be loaded directly on to ones computer, it is a relatively short problem.
- P6-16. Fairly straight forward solution with POLYMATH or MatLab. This problem is a simpler version of P6-18. Allows for a small degree of open-endedness in part (c).
- P6-17. This problem is unique in that is one of the few problems with gas phase multiple reactions in which there is a change in the total number of moles. CDP6-H, CDP6-I, and CDP6-J extend this problem.
- P6-18. More complicated version of P6-14, however it is quite straight forward when using POLYMATH.
- P6-19. California Registration Exam Problem.
- P6-20. Short problem using living example problem E6-8.
- P6-21. Many reactions are shown. The point is to find which ones are dominate at what temperatures. Usually assigned at graduate level in conjunction with PSSH in Chapter 7.
- P6-22. Requires the student to go outside the text to develop an original problem.
- P6-23. New problem with recent (1996) real data for a gas phase reaction with a change in the total number of moles. It is open-ended in that it asks the student to select the best feed conditions.
- P6-24. Member Problem Hall of Fame. This problem is designed to help enhance the students critical thinking and creative thinking skills by varying the feed temperature and concentrations to maximize methanol production. Should count for more than one assignment.
- P6-25. This current (1996) problem is quite open-ended and probably be assigned only at the senior or gradate level. Real reactions and real numbers.
- P6-26. This problem is more straight forward than P6-24 and P6-25 and can rapidly be solved with POLYMATH.

- P6-27.** This problem requires the use of Attainable Region Analysis (ARA) to solve it and in fact is solved on the web.
- CDP6-A** Maximize S for parallel reactions. Alternative to problems P6-4, CDP6-B.
- CDP6-B** Rework of P6-14 for different reaction order. Alternative to problems P6-4, CDP6-A.
- CDP6-C** Straight forward. Alternative to P6-14.
- CDP6-D** Straight forward.
- CDP6-E** Simpler alternative to P6-9.
- CDP6-F** Very straight forward problem to reinforce the principles.
- CDP6-G** Requires additional reading.
- CDP6-H** Good problem involving gas phase reactions with a change in the number of moles. Straight forward.

Problems CDP6-I and CDP6-J are extensions of Problem CDP6-H.

- CDP6-K** Have not assigned this graduate level problem.
- CDP6-L** Have not assigned this graduate level problem.
- CDP6-M** Straight forward. Alternative to F.
- CDP6-N** Graduate level problem has yet to be assigned.
- CDP6-O** Straight forward.
- CDP6-P** Graduate level problem yet to be assigned.

Summary

	<u>Assigned</u>	<u>Alternates</u>	<u>Difficulty</u>	<u>Time</u>	<u>Solution Given</u>
P6-1				20	No
P6-2				70	No
P6-3	G		SF	50	Yes
P6-4	AA	6,A,C,D		60	Yes
P6-5	G	3		60	Yes
P6-6	AA	4,10,12,C		45	Yes
P6-7		7	SF	50	Yes
P6-8		8	SF	75	Yes
P6-9	G	E		120	Yes

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P6-10	I	4,6	35	Yes
● P6-11			40	Yes
P6-12	I	6,10,15,23	30	Yes
● P6-13		17	75	Yes
P6-14	AA	16,B,C	75	Yes
P6-15	AA	6,10,12,M	60	Yes
P6-16	AA	14,18	45	Yes
● P6-17	AA	13,H,I,J	25	Yes
P6-18	AA	14,C,N	35	Yes
P6-19	I		40	Yes
P6-20	O		30	Yes
P6-21	G		90	No
P6-22	S			No
● P6-23	AA	12,23,24,25,25,K,L	40	Yes
P6-24	AA	23,25,26,K,L	60	Yes
P6-25	AA	23,24,26,K,L	90	No
P6-26	AA	23,24,25,K,L	75	Yes
P6-27	G		45	No
CDP6-A	AA	4,C,D	30	Yes
CDP6-B	AA	16	45	Yes
CDP6-C	AA	6,12,14,18,A,D	55	Yes
CDP6-D	O	C	45	Yes
CDP6-E	O	9	30	Yes
CDP6-F	O	12	45	Yes
CDP6-G	G	—	70	Yes
CDP6-H	AA	13,17	30	Yes
CDP6-I	AA	13,17	30	Yes
CDP6-J	AA	13,17	30	Yes
CDP6-K	G	23,24,25,26	60	Yes
CDP6-M	O		45	Yes
CDP6-N	G		90	Yes
CDP6-Q			60	Yes

Assigned

- = Always assigned, AA = Always assign one from the group of alternates, O = Often, I = Infrequently, S = Seldom, G = Graduate level

Alternates

In problems that have a dot in conjunction with AA means that one of the problems, either the problem with a dot or any one of the alternates are always assigned.

Time

Approximate time in minutes it would take a B/B* student to solve the problem.

Difficulty

SF = Straight forward reinforcement of principles (plug and chug)

FSF = Fairly straight forward (requires some manipulation of equations or an intermediate calculation).

IC = Intermediate calculation required

M = More difficult

OE = Some parts open-ended.

*Note the letter problems are found on the CD-ROM. For example A \equiv CDP1-A.

Summary Table Ch-6

	Equilibrium	Maximize	Batch Reactor	PFR	PBR	CSTR	Semibatch Reactor	Other
Series Reactions	3,5	9(b,c)	9,7,8,E			9		9
Parallel Reactions		6(d),A		13	12	6,12,13,A	13	6
Complex Reaction		M	P,C,25	15,16,17,B,H,I,J,24	N	11,10,20,19,18,H,?,P,23		
Straight Forward Reinforcement of Principles		6a	8(a),9(a,c)	15(a),G,M	12(a),14(d)	11,14(b,c),F,M		
Fairly Straight Forward		6(b)		13(a,b),16(a),18(a)	14(f)		13(c),18(b)	
Parameter Variation		4(c),5(c),6(c,d),10(b),25	9(c,f)	14(a),15(b,c,d),16(a,b)	12(b),13(d),15(b),16(a)	4(c),14(a)		
Open-ended		8(b,d),25,N		16(b)	9(g),17(d)	4(e),6(d)	4(c)	
Critical Thinking		8(c)		16(c),N(e)		N(e)		N
More Difficult		9(b),N	9(b)	10(a),16(b)	N	10(a)	N	

Chapter 6

P6-1 No solution will be given.

P6-2 No solution will be given.

P6-3

The equilibrium constant for the reaction



can be estimated as a function of temperature from the mole fraction data below 100°C.

$$K_p = \frac{y_{\text{cs}}}{y_{\pi}}$$

$$\frac{d \ln K_p}{d(1/T)} = \frac{\Delta H_R}{R}$$

T	523	375	} \frac{-1.39 - (-1.11)}{3.09 - 2.68} \times 1000 = -683 = \frac{\Delta H_R}{R}
y_{π}	.8	.75	
y_{cs}	.2	.25	
K_p	.25	.33	
$\ln K_p$	-1.39	-1.11	
1000/T	3.09	2.68	

$$\Delta H = -1.357 \frac{\text{cal}}{\text{mol}}$$

P6-4

a)



$$r_D = 800e^{-2000/T} C_A^{0.5} C_C$$



$$r_{U_1} = 10e^{-300/T} C_A C_C$$

$$S_{DU_1} = \frac{r_D}{r_{U_1}} = 80 C_A^{-0.5} e^{-1700/T}$$

To maximize S_{DU_1} ,

- Operate at high temperatures
- C_A should be kept low
- Tubular reactor with side streams of A
- Semi-batch reactor with A fed slowly into a solution of C

b)



$$r_{U_2} = 1000e^{-8000/T} C_C C_D$$

$$S_{DU_2} = 0.8 \frac{C_A^{0.5}}{C_D} e^{6000/T}$$

T (K)	$S_{DU_1} C_A^{0.5}$	$S_{DU_2} C_D / C_A^{0.5}$
273	0.158	2.805×10^9
473	2.198	2.583×10^9
873	11.412	7.725×10^2
1000	14.614	322.74
1250	20.532	97.208
1500	25.756	43.678
1750	30.283	24.616
2000	34.193	16.068

Hence to minimize selectivity we can use two reactors

1st CSTR: 2000K

2nd CSTR: 1250 K

c)

$$V = \frac{F_{D0} - F_D}{-r_D}; F_D = r_D V$$

$$V = \frac{F_{A0} - F_A}{-r_A}; F_A = F_{A0} + r_A V$$

$$Y_D = \frac{F_D}{F_{A0} - F_A} = \frac{r_D V}{-r_A V} = \frac{r_D}{-r_A}$$

$$r_A = -800e^{-2000/T} C_A^{0.5} C_C - 10e^{-300/T} C_A C_C$$

$$r_D = 800e^{-2000/T} C_A^{0.5} C_C - 1000e^{-8000/T} C_D C_C$$

$$C_A v_0 = F_A; v_0 = 1 \frac{dm^3}{min}, C_A = F_A$$

$$C_A - C_{A0} + 2r_A$$

$$C_D = 2r_D$$

$$C_C = C_{C0} + 2r_C$$

$$r_C = r_A - 1000e^{-8000/T} C_D C_C$$

Using these equations in POLYMATH for different inlet concentrations, yield is maximized at different temperatures

P6-4 (cont'd)

e.g.

T	C_{CO} (mol/dm ³)	Yield
850	1	0.977
500	0.5	0.987
1300	2	0.96

6-4 (c)

Equations:

$$f(ca) = ca - cao - 2 \cdot ra$$

$$f(cd) = cd - 2 \cdot rd$$

$$f(cc) = cc - cco - 2 \cdot xc$$

$$cao = 1$$

$$cco = 0.5$$

$$T = 1300$$

$$ra = -800 \cdot \exp(-2000/T) \cdot ca^{0.5} \cdot cc - 10 \cdot \exp(-300/T) \cdot ca \cdot cc$$

$$rd = 800 \cdot \exp(-2000/T) \cdot ca^{0.5} \cdot cc - 1000 \cdot \exp(-8000/T) \cdot cd \cdot cc$$

$$xc = ra - 1000 \cdot \exp(-8000/T) \cdot cc \cdot cd$$

$$y = rd / -ra$$

Initial value

1

0

0.5

All maximum yields greater than 0.95.

Lower concentration \rightarrow higher temperatures to get right yield. See POLYMATH solution below.

d)



$$-r_A = k_1 C_A; k_1 = 10 \text{ sec}^{-1}$$



$$-r_C = k_2; k_2 = 0.03 \frac{\text{lbmol}}{\text{ft}^3 \text{ sec}}$$

$$F_T = 10 \text{ lbmol/sec}$$

$$\frac{dF_A}{dV} = r_A = -k_1 C_A$$

$$F_A = C_A v_0$$

$$C_{T0} = \frac{0.5}{0.73 \cdot 900} = 7.61 \cdot 10^{-6}$$

$$\therefore v_0 = 13140$$

$$V = 1005 \text{ ft}^3$$

See POLYMATH solution below

P6-4 (cont'd)

6-4 (d)

Equations:

$$d(fa)/d(V)=ra$$

$$d(fc)/d(V)=rc$$

$$d(fb)/d(V)=-ra$$

$$d(fd)/d(V)=-rc$$

$$d(fe)/d(V)=-rc$$

$$k1=10$$

$$k2=.03$$

$$ft=fa+fc+fb+fd+fe$$

$$fao=5$$

$$cto=5/(900^{.73})$$

$$fto=10$$

$$rc=-k2$$

$$x=(fao-fa)/fao$$

$$avo=fto/cto$$

$$ca=cto*(fa/ft)$$

$$ra=-k1*ca$$

Initial value

5

5

0

0

0

6-4 (d)

<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
V	0	105	0	105
fa	5	5	2.49621	2.49621
fc	5	5	1.85	1.85
fb	0	2.50379	0	2.50379
fd	0	3.15	0	3.15
fe	0	3.15	0	3.15
k1	10	10	10	10
k2	0.03	0.03	0.03	0.03
ft	10	13.15	10	13.15
fao	5	5	5	5
cto	0.00761035	0.00761035	0.00761035	0.00761035
fto	10	10	10	10
rc	-0.03	-0.03	-0.03	-0.03
x	0	0.500758	0	0.500758
avo	1314	1314	1314	1314
ca	0.00380518	0.00380518	0.00144464	0.00144464

a) Using the equation for the equilibrium constants:

$$K_{c1} = \frac{C_C C_D}{C_A C_B} \quad K_{c2} = \frac{C_X C_Y}{C_C C_B}$$

We can come up with the equations for C_A , C_D , and C_X .

$$C_A = \frac{C_C C_D}{K_{c1} C_B}$$

$$C_D = \frac{K_{c1} C_A C_B}{C_C}$$

$$C_X = \frac{K_{c2} C_C C_B}{C_Y}$$

The rest can be found with stoichiometry.

$$C_Y = C_X$$

$$C_B = C_{B0} - C_D - C_Y$$

$$C_C = C_{A0} - C_A - C_X$$

POLYMATH

6-5 a

Equations:

$$f(ca) = ca - cc \cdot cd / (K1 \cdot cb)$$

$$f(cd) = cd - K1 \cdot ca \cdot cb / cc$$

$$f(cx) = cx - K2 \cdot cc \cdot cb / cy$$

$$K1 = 4$$

$$K2 = 1$$

$$cy = cx$$

$$cbo = 1.5$$

$$cao = 1.5$$

$$cc = cao - ca - cx$$

$$x = (cao - ca) / cao$$

$$cb = cbo - cd - cy$$

6-5 a

Solution

Variable	Value	f()
ca	0.0306182	3.049e-19
cd	0.109652	-1.084e-18
cx	0.714386	-1.105e-16
K1	4	
K2	1	
cy	0.714386	
cbo	1.5	
cao	1.5	
cc	0.754995	
x	0.979538	
cb	0.675961	

$$C_A = 0.0306 \quad C_B = 0.68 \quad C_C = 0.75 \quad C_D = 0.11$$

$$C_X = 0.71 \quad C_Y = 0.71$$

We also find that $X = 0.98$

P6-5 cont'd

b) With the new equation we must find the new equilibrium equations.

$$C_Z = K_{c3} C_A C_X$$

$$C_Y = \frac{K_{c2} C_C C_B}{C_X}$$

$$C_D = \frac{K_{c1} C_A C_B}{C_C}$$

The rest are the same except for:

$$C_X = C_Y - C_Z$$

$$C_A = C_{A0} - C_D - C_Z$$

6-5

Equations:

$$f(cz) = cz - k3 \cdot ca \cdot cx$$

$$f(cy) = cy - k2 \cdot cc \cdot cb / cx$$

$$f(cd) = cd - k1 \cdot ca \cdot cb / cc$$

$$k3 = 5$$

$$cx = cy - cz$$

$$k2 = 1.51$$

$$k1 = 2.63$$

$$cao = 1.5$$

$$cbo = 1.5$$

$$sdz = cd / cz$$

$$syz = cy / cz$$

$$ca = cao - cd - cz$$

$$cb = cbo - cd - cy$$

$$cc = cao - ca - cx$$

$$scx = cc / cx$$

Variable	Value	f()
cz	0.990725	1.092e-13
cy	1.07384	1.144e-12
cd	0.268101	-2.607e-15
cx	0.0831135	
cao	1.5	
cbo	1.5	
T	300	
sdz	0.270611	
syz	1.08389	
k3	49.4255	
ca	0.241174	
k2	0.480271	
cb	0.15806	
k1	8.26888	
x	0.839217	
cc	1.17571	
scx	14.1459	

We find that

$$C_Z = 0.65$$

$$C_Y = 0.91$$

$$C_D = 0.37$$

$$C_X = 0.27$$

$$C_A = 0.48$$

$$C_B = 0.22$$

$$C_C = 0.76$$

$$X = 0.68$$

$$S_{CX} = 2.8$$

$$S_{DZ} = 0.57$$

$$S_{YZ} = 1.41$$

c) When the temperature is raised from 300 K to 500 K, S_{CX} goes down, S_{DZ} goes up and S_{YZ} goes up.

d) First find the proportionality constants from the Arrhenius equation.

$$0.002 = A_1 e^{-(10000/(1.987 \cdot 300))}$$

$$A_1 = 38603$$

$$0.06 = A_2 e^{-(20000/(1.987 \cdot 300))}$$

$$A_2 = 2.24 \times 10^{13}$$

$$0.3 = A_3 e^{-(30000/(1.987 \cdot 300))}$$

$$A_3 = 2.16 \times 10^{21}$$

Once those are known, come up with equations for the equations in terms of

space-time τ .

$$\tau = \frac{C_{A0} - C_A}{k_1 + k_2 C_A + k_3 C_A^2}$$

$$\tau k_1 + \tau k_2 C_A + \tau k_3 C_A^2 - C_{A0} + C_A = 0$$

$$C_A = \frac{-(\tau k_2 + 1) + \sqrt{(\tau k_2 + 1)^2 - 4(\tau k_3)(\tau k_1 - C_{A0})}}{2\tau k_3}$$

$$\tau = \frac{-C_X}{-k_1}$$

$$\tau = \frac{-C_B}{k_2 C_A}$$

$$\tau = \frac{-C_Y}{-k_3 C_A^2}$$

$$C_X = k_1 \tau$$

$$C_B = k_2 \tau C_A$$

$$C_Y = k_3 \tau C_A^2$$

Use EXCEL solver in order to find the temperature that maximizes C_B .

T
312.5336841

Ca
0.016513937

k1
0.003919233

Cx
0.039192325

k2
0.230891512

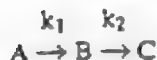
Cb
0.038129279

k3
2.260443602

Cy
0.006164458

P6-7 US legal limit: 1 g/l

Sweden legal limit: 0.5 g/l



$$\frac{dC_A}{dt} = -k_1 C_A ; k_1 = 10 \text{ hr}^{-1} ; A = \text{Alcohol in gastrointestinal tract}$$

$$\frac{dC_B}{dt} = -k_2 + k_1 C_A ; k_2 = 0.192 \frac{\text{g}}{\text{l-hr}} ; B = \text{Alcohol in blood}$$

$$C_A = C_{A0} e^{-k_1 t}$$

$$\frac{dC_B}{dt} = k_1 C_{A0} e^{-k_1 t} - k_2$$

$$C_B = -C_{A0} e^{-k_1 t} - k_2 t + C$$

$$\text{If at } t=0 ; C_B=0 \Rightarrow C = C_{A0}$$

$$C_B = C_{A0} (1 - e^{-k_1 t}) - k_2 t$$

$$\text{or if at } t=0 ; C_B = C_{B0} \Rightarrow C = C_{A0} + C_{B0}$$

$$C_B = C_{A0} (1 - e^{-k_1 t}) + C_{B0} - k_2 t$$

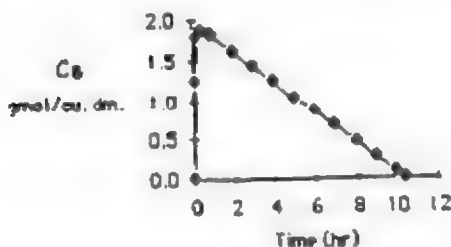
(a) Two tall martinis = 80 g ETOH

Body fluid = 40 l

$$C_{A0} = \frac{80 \text{ g}}{40 \text{ l}} = 2 \text{ g/l}$$

$$\text{At } t=0 ; C_B=0 ; C_B = C_{A0} (1 - e^{-k_1 t}) - k_2 t$$

$$C_B = 2 \frac{\text{g}}{\text{l}} (1 - e^{-10t}) - 0.192t \text{ where } t \text{ in hours}$$



In U.S. for $C_B = 1 \frac{\text{g}}{\text{l}}$. $t = 5.2$ hrs

6-14

P6-7 (cont'd)

$$(f) \quad 60 \text{ g immediately} \Rightarrow C_{A0} = 1.5 \frac{\text{g}}{\text{l}}$$

$$C_B = C_{A0} (1 - e^{-k_1 t}) - 0.192t$$

$$C_B = 1.5 (1 - e^{-0.15t}) - 0.192t$$

$$C_B = 1 \frac{\text{g}}{\text{l}} \text{ at } t = 0.115 \text{ hr at } t = 2.6 \text{ hr}$$

(23g) A heavy person would be less affected by the alcohol than a thin one. That is, the reaction rate constant would be lower for a heavy person.

P6-8

(a)

Let A be the tarzlon in the stomach and B be the tarzlon in the blood.

Mole Balances:

$$\frac{dC_A}{dt} = r_A$$

$$\frac{dC_B}{dt} = r_B$$

Rate Laws:

$$-r_A = k_1 C_A + k_2 C_A$$

$$r_B = k_1 C_A - k_3 - k_4 C_B$$

All k values are given in the problem statement. It must be noted, however, that for $C_B < 0$, k_3 must be equal to 0.

These equations when entered in POLYMATH generate the following results:

Equations:

$$d(ca)/d(t) = -k_1 ca - k_2 ca$$

$$d(cb)/d(t) = k_1 ca - k_3 - k_4 cb$$

$$k_1 = 0.15$$

$$k_2 = 0.6$$

$$k_4 = 0.2$$

$$k_3 = \text{if}(cb < 0) \text{ then}(k_1 ca - k_4 cb) \text{ else}(0.1)$$

$$t_0 = 0, \quad t_f = 24$$

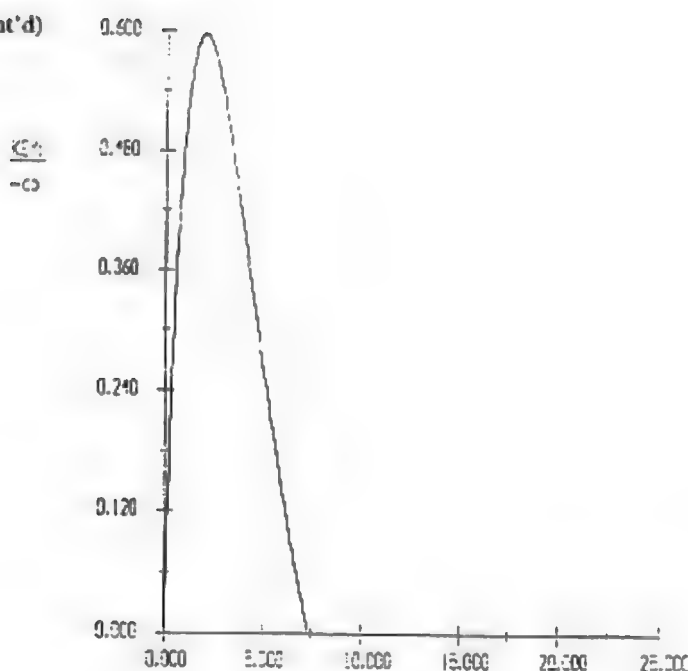
Initial value

6.25

0

6-15

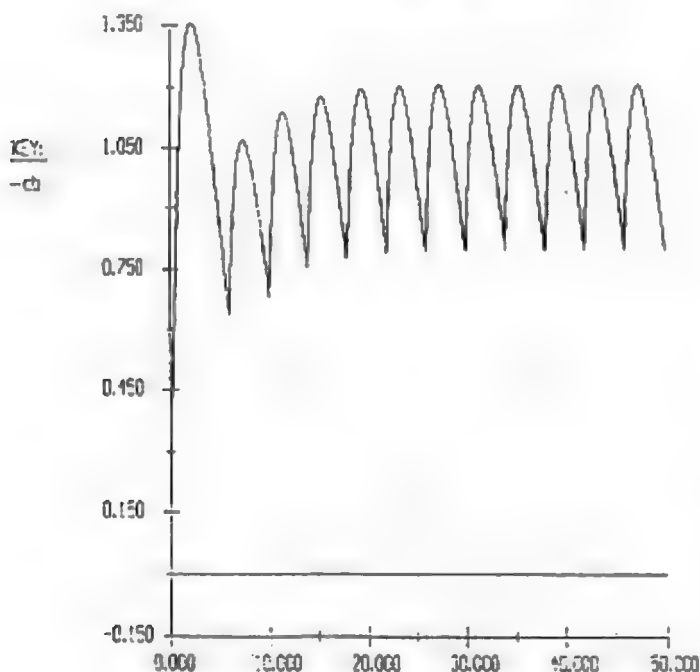
P6-8 (cont'd)



(b)

From the following graph generated using the above program in POLYMATH, we can see the proper doses of the drug:

1. First take two doses of the drug.
2. Six hours later take one dose.
3. Take one dose every four hours from then on.



a) Species A:

$$\frac{dC_A}{dt} = r_A$$

$$-r_A = k_1 C_A$$

Species B:

$$\frac{dC_B}{dt} = r_B$$

$$r_B = k_1 C_A - k_2 C_B$$

Species C:

$$\frac{dC_C}{dt} = r_C$$

$$r_C = k_2 C_B$$

Plugging into POLYMATH: gets the following.

Equations:

$$d(ca)/d(t) = ra$$

$$d(cb)/d(t) = rb$$

$$d(cc)/d(t) = rc$$

$$k1 = .4$$

$$k2 = .01$$

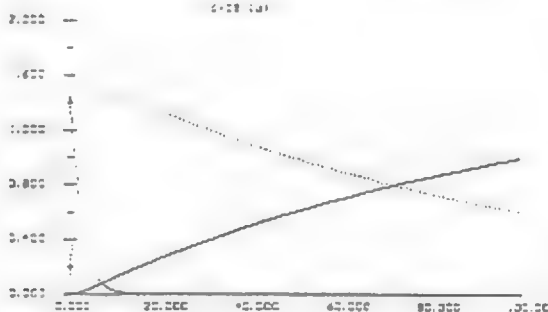
$$ra = -k1 * ca$$

$$rc = k2 * cb$$

$$rb = k1 * ca - k2 * cb$$

$$t_0 = 0, \quad t_f = 100$$

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	100	0	100
ca	1.6	1.6	6.7898e-18	6.7898e-18
cb	0	1.4556	0	0.6037
cc	0	0.9963	0	0.9963
k1	0.4	0.4	0.4	0.4
k2	0.01	0.01	0.01	0.01
ra	-0.64	-2.71592e-18	-0.64	-2.71592e-18
rc	0	0.014556	0	0.006037
rb	0.64	0.64	-0.0132417	-0.006037



b) To find the maximum profit, take the above equations and add this one:

$$\text{Cost} = 50 * C_B * 500 - 10 * C_A * 500 - 50 * C_A * 500 - 30 * (e^{(3 * C_C)} - 1)$$

Plugging into POLYMATH: gets the following.

P6-9 cont'd

Equations:

$$d(ca)/d(t) = ra$$

$$d(cb)/d(t) = rb$$

$$d(cc)/d(t) = rc$$

$$k1 = .4$$

$$k2 = .01$$

$$Co = 50 * cb * 500 - 10 * ca * 500 - 50 * ca * 500 - 30 * (\exp(.5 * cc * 500) - 1)$$

$$ra = -k1 * ca$$

$$rc = k2 * cb$$

$$rb = k1 * ca - k2 * cb$$

$$t_0 = 0, \quad t_f = 4$$

Initial value

1.6

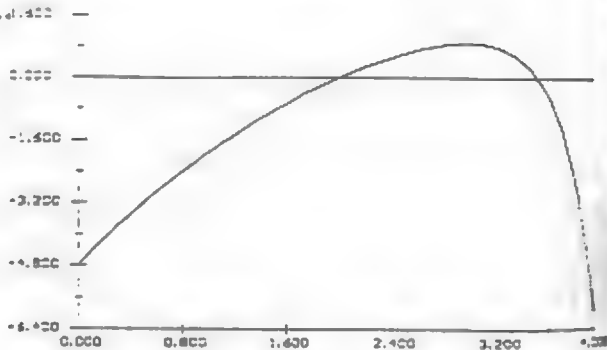
0

0

Scale: 10⁻⁴

$\frac{d(f)}{dt}$

-20



Variable	Initial value	Maximum value	Minimum value	Final value
t	0	4	0	4
ca	1.6	1.6	0.323034	0.323034
cb	0	1.24536	0	1.24536
cc	0	0.0316028	0	0.0316028
k1	0.4	0.4	0.4	0.4
k2	0.01	0.01	0.01	0.01
Co	-48000	8784.85	-59502.7	-59502.7
ra	-0.64	-0.129214	-0.64	-0.129214
rc	0	0.0124536	0	0.0124536
rb	0.64	0.64	0.11676	0.11676

Find the maximum profit occurs at $t=3.2$ h

c) First, find the values for the proportionality constant from the Arrhenius equation.

$$0.4h^{-1} = 0.0001s^{-1}$$

$$0.01h^{-1} = 2.78 \times 10^{-6}s^{-1}$$

$$0.0001 = A_1 e^{-(10000/(1.987 \cdot 373))}$$

$$A_1 = 72$$

$$2.78 \times 10^{-6} = A_2 e^{-(20000/(1.987 \cdot 373))}$$

P6-9 cont'd

Using the CSTR design equation with respect to space-time, come up with equations for C_A and C_B .

$$\tau = \frac{C_{A0} - C_A}{k_1 C_A}$$

$$C_A = \frac{C_{A0}}{1 + \tau k_1}$$

$$\tau = \frac{-C_B}{-k_1 C_A + k C_B}$$

$$C_B = \frac{k_1 \tau C_A}{\tau k_2 + 1}$$

Using EXCEL's solver, come up with the temperature that maximizes B. The concentration and temperature are shown below.

T	k1
437.941035	0.0007354
k2	Ca
0.00015231	0.68854972
Cb	
0.7153319	

d) Part d is similar to part b except for two rate laws:

$$r_A = k_{-1} r * C_B - k_1 * C_A$$

$$r_B = k_1 * C_A - k_{-1} * C_B - k_2 * C_B$$

Using those rate laws in POLYMATH produce the following:

Equations:

$$d(ca)/d(t) = ra$$

$$d(cb)/d(t) = rb$$

$$d(cc)/d(t) = rc$$

$$k1r = 8.33e-5$$

$$k1f = .0001$$

$$k2 = 2.78e-6$$

$$rc = k2 * cb$$

$$ra = k1r * cb - k1f * ca$$

$$rb = k1f * ca - k1r * cb - k2 * cb$$

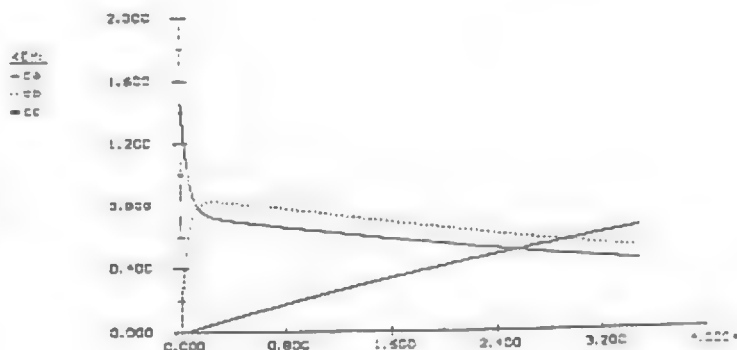
$$t_0 = 0, \quad t_f = 350000$$

Initial value

1.6

0

0



P6-9 cont'd

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	350000	0	350000
ca	1.6	1.6	0.436316	0.436316
cb	0	0.833237	0	0.5159
cc	0	0.647784	0	0.647784
k1r	8.33e-05	8.33e-05	8.33e-05	8.33e-05
k1f	0.0001	0.0001	0.0001	0.0001
k2	2.78e-06	2.78e-06	2.78e-06	2.78e-06
rc	0	2.3164e-06	0	1.4342e-06
ra	-0.00016	-6.57168e-07	-0.00016	-6.57168e-07
rb	0.00016	0.00016	-1.20632e-06	-7.77034e-07

e) Part e is similar to part d except for one rate law:

$$r_c = k_2 * C_B - k_{-2} * C_c$$

Using that in POLYMATH produces the following:

Equations:

$$d(ca)/d(t)=ra$$

$$d(cb)/d(t)=rb$$

$$d(cc)/d(t)=rc$$

$$k1r=8.33e-5$$

$$k1f=.0001$$

$$k2f=2.78e-6$$

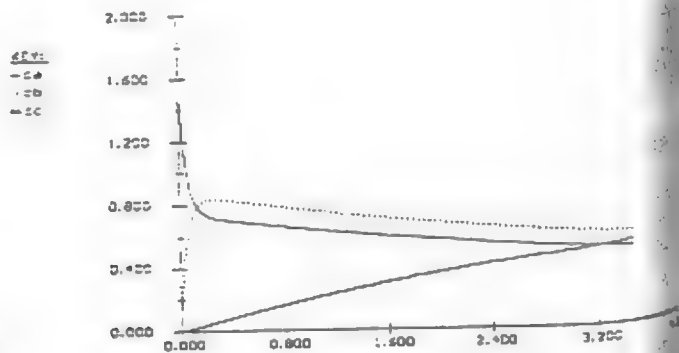
$$k2r=1.39e-6$$

$$ra=k1r*cb-k1f*ca$$

$$rc=k2f*cb-k2r*cc$$

$$rb=k1f*ca-k1r*cb-k2f*cb+k2r*cc$$

$$t_0 = 0, \quad t_f = 350000$$



Variable	Initial value	Maximum value	Minimum value	Final value
t	0	350000	0	350000
ca	1.6	1.6	0.490306	0.490306
cb	0	0.833769	0	0.583662
cc	0	0.526032	0	0.526032
k1r	8.33e-05	8.33e-05	8.33e-05	8.33e-05
k1f	0.0001	0.0001	0.0001	0.0001
k2f	2.78e-06	2.78e-06	2.78e-06	2.78e-06
k2r	1.39e-06	1.39e-06	1.39e-06	1.39e-06
ra	-0.00016	-4.11573e-07	-0.00016	-4.11573e-07
rc	0	2.25569e-06	0	8.91396e-07
rb	0.00016	0.00016	-1.12493e-06	-4.79824e-07

6-20

P6-9 cont'd

f) When $k_1 > 100$ and $k_2 < 0.1$ the concentration of B immediately shoots up to 1.6 and then slowly comes back down, while CA drops off immediately and falls to zero. This is because the first reaction is so fast and the second reaction is slower with no reverse reactions.

When $k_2 = 1$ then the concentration of B spikes again and remains high, while very little of C is formed. This is because after B is formed it will not go to C because the reverse reaction is faster.

When $k_2 = 0.25$, B shoots up, but does not stay as high because the second reverse reaction is a slightly slower than seen before, but still faster than the forward reaction.

g)

$$\frac{dF_A}{dW} = r_A'$$

$$r_A' = -k_1 C_A$$

$$C_A = \frac{N_A}{v}$$

$$v = v_0 \left(\frac{P_0}{P} \right)$$

$$\left(\frac{P_0}{P} \right) = (1 - \alpha W)^{1/2}$$

Combining:

$$\frac{dF_A}{dW} = \frac{-k_1 F_A (1 - \alpha W)^{1/2}}{v_0}$$

Similarly:

$$\frac{dF_B}{dW} = r_B$$

$$r_B = k_1 C_A - k_2 C_B$$

$$C_A = \frac{F_A}{v}$$

$$C_B = \frac{F_B}{v}$$

$$\frac{dF_B}{dW} = \frac{k_1 F_A (1 - \alpha W)^{1/2} - k_2 F_B (1 - \alpha W)^{1/2}}{v_0}$$

and:

$$\frac{dF_C}{dW} = \frac{k_2 F_B (1 - \alpha W)^{1/2}}{v_0}$$

Once those are done we have to come up with a way to change α with the change in diameter of the particle. We know that

$$\alpha = J \beta_0$$

$$J = \frac{2}{A_c \rho_c (1 - \phi) P_0}$$

$$\beta_0 = \frac{L}{D_p} \left[\frac{M}{D_p} + N \right]$$

Where J, L, M, and N are constants that won't change for this problem.

Starting at the given α and the following chart was made.

P6-9 cont'd

Equations:

$$d(fc)/d(w) = k2 \cdot fb \cdot (1 - \alpha p \cdot w)^{-0.5} / v_o$$

$$d(fb)/d(w) = (k1 \cdot fa \cdot (1 - \alpha p \cdot w)^{-0.5} - k2 \cdot fb \cdot (1 - \alpha p \cdot w)^{-0.5}) / v_o$$

$$d(fa)/d(w) = -k1 \cdot fa \cdot (1 - \alpha p \cdot w)^{-0.5} / v_o$$

$$k1 = .25$$

$$k2 = .15 \quad 6-09g \quad dp=1$$

$$\alpha p = .00098$$

$$v_o = 10$$

$$fa0 = 10.0000001$$

$$Sbc = fb / fc$$

$$Yb = fb / (fa0 - fa)$$

Initial value

1e-06

0

10

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	100	0	100
fc	1e-06	5.51973	1e-06	5.51973
fb	0	4.64738	0	3.60664
fa	10	10	0.873606	0.873606
k1	0.25	0.25	0.25	0.25
k2	0.15	0.15	0.15	0.15
alp	0.00098	0.00098	0.00098	0.00098
vo	10	10	10	10
fa0	10	10	10	10
Sbc	0	177.571	0	0.65342
Yb	0	0.994405	0	0.39522

When D_p increases to 2 cm, according to the above equations, β_0 decreases by 3/4 and α also decreases by 3/4. The following chart was made and the selectivity has gone down.

6-09g dp=2

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	100	0	100
fc	1e-06	5.55377	1e-06	5.55377
fb	0	4.64749	0	3.5863
fa	10	10	0.859935	0.859935
k1	0.25	0.25	0.25	0.25
k2	0.15	0.15	0.15	0.15
alp	0.000735	0.000735	0.000735	0.000735
vo	10	10	10	10
fa0	10	10	10	10
Sbc	0	177.527	0	0.645741
Yb	0	0.994403	0	0.392371

6-22

P6-9 cont'd

When D_p decreases to 0.5, according to the above equations, β_0 increases by 6 and α also increases by 6. The following chart was made and the selectivity goes up.

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	100	0	100
fc	1e-06	4.70888	1e-06	4.70888
fb	0	4.64701	0	4.04792
fa	10	10	1.24321	1.24321
k1	0.25	0.25	0.25	0.25
k2	0.15	0.15	0.15	0.15
alp	0.00588	0.00588	0.00588	0.00588
vo	10	10	10	10
fa0	10	10	10	10
Sbc	0	52.6414	0	0.859635
Yb	0	0.981359	0	0.46226

Therefore choose the smallest particle and the selectivity will be high.

P6-10

(a)

Mole Balances: $\frac{dF_A}{dV} = -r_B - r_C$ $\frac{dF_B}{dV} = r_B$ $\frac{dF_C}{dV} = r_C$

Rate Laws: $r_B = k_1 C_A^2$ $k_1 = 15$
 $r_C = k_2 C_A$ $k_2 = 0.015$

Stoichiometry: $C_A = C_{T0} \left(\frac{F_A}{F_T} \right)$ $F_T = F_A + F_B + F_C$

$S = 60F_B - 15F_C - 10F_{A0}$

Use these equations in POLYMATH to find the necessary volume to maximize S.
 $V = 1425 \text{ ft}^3$

P6-10 (cont'd)

Equations:

$$d(fb)/d(V) = r_b$$

$$d(fa)/d(V) = -r_c - r_b$$

$$d(fc)/d(V) = r_c$$

$$cao = 0.00447$$

$$k_1 = 15$$

$$k_2 = 0.015$$

$$ft = fa + fb + fc$$

$$fao = 0.06705$$

$$cost = 60 \cdot fb - 15 \cdot fc - 10 \cdot fao$$

$$ca = cao \cdot (fa/ft)$$

$$rc = k_2 \cdot ca$$

$$rb = k_1 \cdot ca^{**2}$$

$$V_0 = 0, \quad V_f = 3000$$

V

$$1012.5$$

$$1050$$

$$1087.5$$

$$1125$$

$$1162.5$$

$$1200$$

$$1237.5$$

$$1275$$

$$1312.5$$

$$1350$$

$$1387.5$$

$$1425$$

$$1462.5$$

$$1500$$

$$1537.5$$

$$1575$$

cost

$$1.4570562$$

$$1.4592956$$

$$1.4611432$$

$$1.4626513$$

$$1.4638652$$

$$1.4648239$$

$$1.4655614$$

$$1.4661071$$

$$1.4664866$$

$$1.4667222$$

$$1.4668335$$

$$1.4668376$$

$$1.4667493$$

$$1.4665818$$

$$1.4663465$$

$$1.4660535$$

(b)

$$\text{Mole Balances:} \quad F_A = F_{A_0} + r_A V \quad F_B = r_B V \quad F_C = r_C V$$

$$\text{Rate Laws:} \quad r_A = -r_B - r_C \quad r_B = k_1 C_A^2 \quad r_C = k_2 C_A$$

$$k_1 = k_{\infty} \exp\left(\frac{E_1}{R}\right) \left(\frac{1}{T} - \frac{1}{919.67}\right) \quad F_i = v_0 C_i$$

$$\$ = v_0 (60C_B - 15C_C - 10C_{A_0})$$

Use these equations in POLYMATH and vary T from 860°R to 1160°R and find maximum value for \$.

\$ steadily rises with temperature and reaches a maximum at 970°R (510.33°F).

P6-10 (cont'd)

Equations:

$$f(ca) = ca - cao - ra \cdot \tau$$

0.00447

$$f(cb) = cb - rb \cdot \tau$$

0

$$f(cc) = cc - rc \cdot \tau$$

0

$$cao = 0.00447$$

$$E1 = 10000$$

$$R = 1.987$$

$$T = 970$$

$$k2o = 0.015$$

$$E2 = 20000$$

$$k1o = 15$$

$$vo = 15$$

$$V = 400$$

$$\tau = V / vo$$

$$cost = vo \cdot (60 \cdot cb - 15 \cdot cc - 10 \cdot cao)$$

$$k1 = k1o \cdot \exp(E1 / R \cdot (1/T - 1/919.67))$$

$$k2 = k2o \cdot \exp(E2 / R \cdot (1/T - 1/919.67))$$

$$rb = k1 \cdot ca \cdot 2$$

$$rc = k2 \cdot ca$$

$$ra = -k1 \cdot ca \cdot 2 - k2 \cdot ca$$

Variable	Value	f()
ca	0.00232126	1.267e-13
cb	0.00162263	-1.267e-13
cc	0.000526208	9.897e-18
cao	0.00447	
E1	10000	
R	1.987	
T	970	
k2o	0.015	
E2	20000	
k1o	15	
vo	15	
V	400	
tau	26.6667	
cost	0.671384	
k1	11.2922	
k2	0.0085009	
rb	6.0846e-05	
rc	1.97328e-05	
ra	-8.05778e-05	

P6-11

a)

$$r_{1A} = -k_{1A} C_A = -(0.07)(.1) = -0.07 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

$$r_{2A} = -\frac{r_{2D}}{3} = -\frac{(.3)(.51)^2(.1)}{3} = -0.0026 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

$$r_{3A} = 0 \cdot r_{3E} = 0 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

b)

$$r_{1B} = \frac{-r_{1A}}{3} = \frac{(.7)(.1)}{3} = 0.023 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

$$r_{2B} = 0 \cdot r_{2D} = 0 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

$$r_{3B} = 0 \cdot r_{3E} = 0 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

c)

$$r_{1C} = \frac{-r_{1A}}{3} = \frac{(.7)(.1)}{3} = 0.023 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

$$r_{2C} = \frac{-2 \cdot r_{2D}}{3} = \frac{-2(.3)(.51)^2(.1)}{3} = -0.0052 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

$$r_{3C} = -r_{3E} = -(0.2)(.049)(.51) = -0.005 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

P6-11 cont'd

d)

$$r_{1D} = 0 * r_{1A} = 0 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

$$r_{2D} = (.3)(.51)^2(.1) = 0.0078 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

$$r_{3D} = \frac{-4r_{3E}}{3} = \frac{-4(.2)(.049)(.51)}{3} = -0.0067 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

e)

$$r_{1E} = 0 * r_{1A} = 0 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

$$r_{2E} = 0 * r_{2D} = 0 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

$$r_{3E} = (.2)(.049)(.51) = 0.005 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

f)

$$r_A = -0.07 - 0.0026 = -0.0726 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

$$r_B = 0.023 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

$$r_C = 0.023 - 0.0052 - 0.005 = 0.0128 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

$$r_D = 0.0078 - 0.033 = 0.0011 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

$$r_E = 0.005 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$$

g)

$$V = \frac{F_{A0} - F_A}{-r_A}$$

$$= \frac{v_0(C_{A0} - C_A)}{-r_A}$$

$$= \frac{100(3 - 0.1)}{0.0726} = 4000 \text{ dm}^3$$

P6-12 (cont'd)

(b)

CSTR

Mole Balances: $F_A = F_{A0} + r_A V$ $F_B = r_B V$ $F_M = r_M V$ $F_P = r_P V$

Rate Laws: $r_A = -C_A(k_1 + k_2)$ $r_B = r_M = k_1 C_A$ $r_P = k_2 C_A$

$$k_1 = k_{10} \exp \frac{E_1}{R} \left(\frac{1}{T} - \frac{1}{946} \right) \quad k_2 = k_{10} \exp \frac{E_2}{R} \left(\frac{1}{T} - \frac{1}{946} \right)$$

Stoichiometry: $F_A = v_0 C_A$ $F_B = v_0 C_B$ $F_M = v_0 C_M$ $F_P = v_0 C_P$

Use these equations in POLYMATH and vary T to maximize the yield of *p*-xylene.

The optimal temperature would be about 1455 K (1182°C).

Equations:

$f(ca) = ca - ca_0 - r_a \cdot \tau$

$f(cb) = cb - r_b \cdot \tau$

$f(cm) = cm - r_m \cdot \tau$

$f(cp) = cp - r_p \cdot \tau$

$ca_0 = 0.0375$

$\tau = 0.5$

$k_{10} = 0.22$

$E_1 = 20000$

$R = 1.987$

$T = 1455$

$k_{20} = 0.71$

$E_2 = 10000$

$yp = cp / (0.0375 - ca)$

$k_1 = k_{10} \exp(E_1/R * (1/T - 1/946))$

$k_2 = k_{20} \exp(E_2/R * (1/T - 1/946))$

$rb = k_1 * ca$

$rm = k_1 * ca$

$rp = k_2 * ca$

$ra = -ca * (k_1 + k_2)$

Initial value

0.0375

0

0

0

Variable	Value	f()
ca	0.0354488	-9.358e-13
cb	9.42926e-05	8.431e-15
cm	9.42926e-05	8.431e-15
cp	0.00195691	-8.008e-13
cao	0.0375	
tau	0.5	
k10	0.22	
E1	20000	
R	1.987	
T	1455	
k20	0.71	
E2	10000	
yp	0.909682	
k1	0.00531394	
k2	0.110408	
rb	0.000188585	
rm	0.000188585	
rp	0.00391383	
ra	-0.00410241	

6-27

P6-13

a) Mole balance:

$$\frac{dC_A}{dV} = \frac{r_A}{v_0}$$

$$\frac{dC_D}{dV} = \frac{r_D}{v_0}$$

$$\frac{dC_B}{dV} = \frac{r_B}{v_0}$$

$$\frac{dC_E}{dV} = \frac{r_E}{v_0}$$

$$\frac{dC_C}{dV} = \frac{r_C}{v_0}$$

$$\frac{dC_F}{dV} = \frac{r_F}{v_0}$$

Rate laws:

$$r_A = -r_{D1} - 3 * r_{E2}$$

$$r_F = r_{F3}$$

$$r_B = -2 * r_{D1} - r_{F3}$$

$$r_{D1} = k_{D1} C_A C_B^2$$

$$r_C = r_{D1} + r_{E2} - r_{F3}$$

$$r_{E2} = k_{E2} C_A C_D$$

$$r_D = r_{D1} - 2 * r_{E2} + r_{F3}$$

$$r_{F3} = k_{F3} C_B C_C^2$$

$$r_E = r_{E2}$$

The equation for the conversion of A is this:

$$X = \frac{C_{A0} - C_A}{C_{A0}}$$

The following is the POLYMATH program to give the graphs

Equations:

$$d(cb)/d(v) = rb/v_0$$

$$d(ca)/d(v) = ra/v_0$$

$$d(cc)/d(v) = rc/v_0$$

$$d(cd)/d(v) = rd/v_0$$

$$d(ce)/d(v) = re/v_0$$

$$d(cf)/d(v) = rf/v_0$$

$$v_0 = 10$$

$$kd1 = .25$$

$$ke2 = .1$$

$$kf3 = 5$$

$$cao = 1.5$$

$$x = (cao - ca) / cao$$

$$rd1 = kd1 * ca * cb^2$$

$$re2 = ke2 * ca * cd$$

$$rf3 = kf3 * cb * cc^2$$

$$re = re2$$

$$rf = rf3$$

$$ra = -rd1 - 3 * re2$$

$$rb = -2 * rd1 - rf3$$

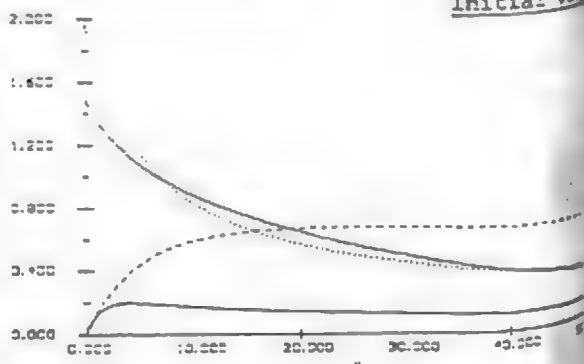
$$rc = rd1 + re2 - 2 * rf3$$

$$rd = rd1 - 2 * re2 + rf3$$

$$v_0 = 0, \quad v_f = 50$$

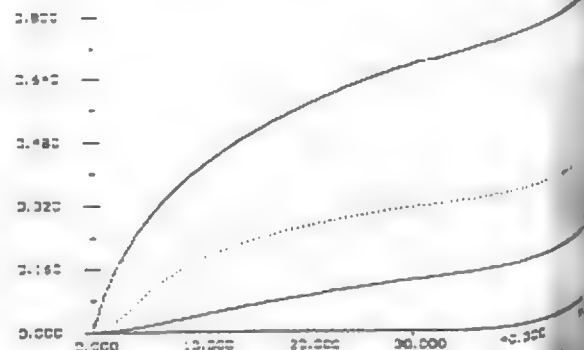
KEY:

— ca
... cb
— cc
-- cd



KEY:

— ce
... cf
— x



P6-13 cont'd

b) With a CSTR, start with the mole balance:

$$F_{A0} - F_A = -r_A V$$

$$F_{B0} - F_B = -r_B V$$

$$F_C = r_C V$$

$$F_D = r_D V$$

$$F_E = r_E V$$

$$F_F = r_F V$$

Next is the relative rate laws and the overall rate laws:

$$\frac{r_{1A}}{-1} = \frac{r_{1B}}{-2} = \frac{r_{1C}}{1} = \frac{r_{1D}}{1} = k_{D1} C_A C_B^2$$

$$\frac{r_{2D}}{-2} = \frac{r_{2A}}{-3} = \frac{r_{2C}}{1} = \frac{r_{2E}}{1} = k_{E2} C_A C_D$$

$$\frac{r_{1B}}{-1} = \frac{r_{2C}}{-2} = \frac{r_{2D}}{1} = \frac{r_{1F}}{1} = k_{F3} C_B C_C^2$$

$$r_A = r_{1A} + r_{2A} = -k_{D1} C_A C_B^2 - 3k_{E2} C_A C_D$$

$$r_B = r_{1B} + r_{2B} = -2k_{D1} C_A C_B^2 - k_{F3} C_B C_C^2$$

$$r_C = r_{1C} + r_{2C} + r_{3C} = k_{D1} C_A C_B^2 + k_{E2} C_A C_D - 2k_{F3} C_B C_C^2$$

$$r_D = r_{1D} + r_{2D} + r_{3D} = k_{D1} C_A C_B^2 - 2k_{E2} C_A C_D + k_{F3} C_B C_C^2$$

$$r_E = r_{2E} = k_{E2} C_A C_D$$

$$r_F = r_{1F} = k_{F3} C_B C_C^2$$

Using stoichiometry, we can then combine it all in terms of conversion and rearrange to be plugged into POLYMATH.

$$F_i = \frac{C_i}{v_0}$$

$$\tau = \frac{V}{v_0}$$

$$f(C_A) = C_A - C_{A0} + (k_{D1} C_A C_B^2 + 3k_{E2} C_A C_D) \tau$$

$$f(C_B) = C_B - C_{B0} + (2k_{D1} C_A C_B^2 + k_{F3} C_B C_C^2) \tau$$

$$f(C_C) = (k_{D1} C_A C_B^2 + k_{E2} C_A C_D - 2k_{F3} C_B C_C^2) \tau - C_C$$

$$f(C_D) = (k_{D1} C_A C_B^2 - 2k_{E2} C_A C_D + k_{F3} C_B C_C^2) \tau - C_D$$

$$f(C_E) = k_{E2} C_A C_D - C_E$$

$$f(C_F) = k_{F3} C_B C_C^2 - C_F$$

That being done we can plug these into POLYMATH and get that $C_A = .61$, $C_B = .79$, $C_C = .11$, $C_D = .45$, $C_E = .45$, $C_F = .14$, $C_F = .25$

P6-13 cont'd

6-13 (b)

Equations:

$$f(ca) = ca - cao - ra \cdot \tau$$

$$f(cb) = cb - cbo - rb \cdot \tau$$

$$f(cc) = rc \cdot \tau - cc$$

$$f(cd) = rd \cdot \tau - cd$$

$$f(ce) = re \cdot \tau - ce$$

$$f(cf) = rf \cdot \tau - cf$$

$$cao = 1.5$$

$$\tau = 50/10$$

$$cbo = 2$$

$$kd1 = .25$$

$$ke2 = .1$$

$$kf3 = 5$$

$$re = ke2 \cdot ca \cdot cd$$

$$rf = kf3 \cdot cb \cdot cc^2$$

$$x = (cao - ca) / cao$$

$$ra = -kd1 \cdot ca \cdot cb^2 - 3 \cdot ke2 \cdot ca \cdot cd$$

$$rb = -2 \cdot kd1 \cdot ca \cdot cb^2 - kf3 \cdot cb \cdot cc^2$$

$$rc = kd1 \cdot ca \cdot cb^2 + ke2 \cdot ca \cdot cd - 2 \cdot kf3 \cdot cb \cdot cc^2$$

$$rd = kd1 \cdot ca \cdot cb^2 - 2 \cdot ke2 \cdot ca \cdot cd - kf3 \cdot cb \cdot cc^2$$

Variable	Value	f()
ca	0.608316	3.608e-16
cb	0.792733	4.563e-16
cc	0.112666	-8.861e-16
cd	0.453528	4.481e-16
ce	0.137944	1.735e-17
cf	0.251565	4.454e-16
cao	1.5	
tau	5	
cbo	2	
kd1	0.25	
ke2	0.1	
kf3	5	
re	0.0275888	
rf	0.050313	
x	0.594456	
ra	-0.178337	
rb	-0.241453	
rc	0.0225331	
rd	0.0907056	

c) For the first case where A is fed into a vat of B. The following equations are the mole balances:

$$\frac{dC_A}{dt} = r_A + v_0 \frac{C_{A0} - C_A}{V}$$

$$\frac{dC_B}{dt} = r_B - v_0 \frac{C_B}{V}$$

$$\frac{dC_C}{dt} = r_C - v_0 \frac{C_C}{V}$$

$$\frac{dC_D}{dt} = r_D - v_0 \frac{C_D}{V}$$

$$\frac{dC_E}{dt} = r_E - v_0 \frac{C_E}{V}$$

$$\frac{dC_F}{dt} = r_F - v_0 \frac{C_F}{V}$$

The rate laws are the same as in part (a) so the only other equation needed is:

$$V = V_0 + v_0 t$$

This gets plugged into POLYMATH:

P6-13 cont'd

Equations:

$$d(ca)/d(t) = ra + vo * (cao - ca) / V$$

$$d(cb)/d(t) = rb - vo * cb / V$$

$$d(cc)/d(t) = rc - vo * cc / V$$

$$d(cd)/d(t) = rd - vo * cd / V$$

$$d(ce)/d(t) = re - vo * ce / V$$

$$d(cf)/d(t) = rf - vo * cf / V$$

$$vo = 10$$

$$cao = 1.5$$

$$Vo = 40$$

$$kd1 = .25$$

$$ke2 = .1$$

$$kf3 = 5$$

$$rd1 = kd1 * ca * cb^2$$

$$re2 = ke2 * ca * cd$$

$$rf3 = kf3 * cb * cc^2$$

$$x = (cao - ca) / cao$$

$$V = Vo + vo * t$$

$$ra = re2$$

$$rb = rf3$$

$$rc = rd1 - 3 * re2$$

$$rd = -2 * rd1 - rf3$$

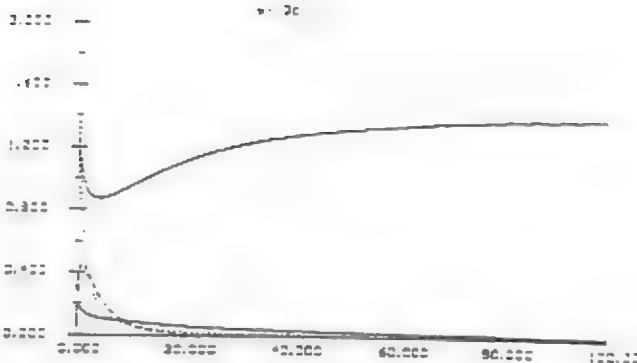
$$re = rd1 + re2 - 2 * rf3$$

$$rf = rd1 - 2 * re2 + rf3$$

$$t_0 = 0, \quad t_f = 100$$

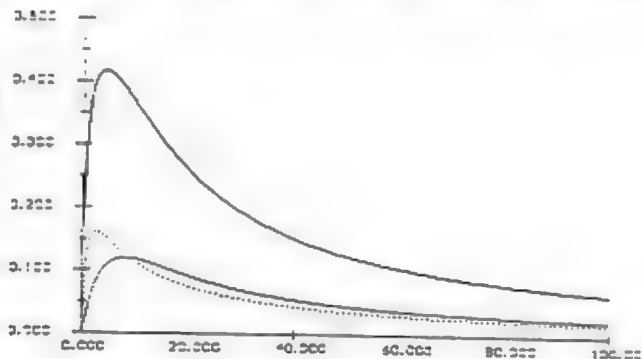
KEY:

— ca
... cb
-- cc
- - cd



KEY:

— ce
... cf
— x



Variable	Initial value	Maximum value	Minimum value	Final value
t	0	100	0	100
ca	1.5	1.5	0.874392	1.40262
cb	2	2	0.00271086	0.00271086
cc	0	0.184965	0	0.0138917
cd	0	0.449824	0	1.99367e-05
ce	0	0.119804	0	0.0231828
cf	0	0.161163	0	0.0185589
vo	10	10	10	10
cao	1.5	1.5	1.5	1.5
Vo	40	40	40	40
kd1	0.25	0.25	0.25	0.25
ke2	0.1	0.1	0.1	0.1
kf3	5	5	5	5
rd1	1.5	1.5	2.57689e-06	2.57689e-06
re2	0	0.0456977	0	2.79638e-06
rf3	0	0.215642	0	2.61569e-06
x	0	0.417072	0	0.0649157
V	40	1040	40	1040
re	0	0.0456977	0	2.79638e-06
rf	0	0.215642	0	2.61569e-06
ra	-1.5	-1.0966e-05	-1.5	-1.0966e-05
rb	-3	-7.76946e-06	-3	-7.76946e-06
rc	1.5	1.5	-0.0128971	1.41886e-07
rd	1.5	1.5	-0.0256529	-4.0018e-07

P6-13 cont'd

For the second case, B is fed into a vat of A. So the following changes to the above design equations are made:

$$\frac{dC_A}{dt} = r_A - v_0 \frac{C_A}{V}$$

$$\frac{dC_B}{dt} = r_B + v_0 \frac{C_{B0} - C_B}{V}$$

All other equations are the same. Again plug into POLYMATH:

6-13c2

Equations:

$$d(ca)/d(t) = ra - v_0 \cdot ca / V$$

$$d(cb)/d(t) = rb + v_0 \cdot (cbo - cb) / V$$

$$d(cc)/d(t) = rc - v_0 \cdot cc / V$$

$$d(cd)/d(t) = rd - v_0 \cdot cd / V$$

$$d(ce)/d(t) = re - v_0 \cdot ce / V$$

$$d(cf)/d(t) = rf - v_0 \cdot cf / V$$

$$v_0 = 10$$

$$cbo = 2$$

$$cao = 1.5$$

$$V_0 = 40$$

$$kd1 = .25$$

$$ke2 = .1$$

$$kf3 = 5$$

$$rd1 = kd1 \cdot ca \cdot cb^2$$

$$re2 = ke2 \cdot ca \cdot cd$$

$$rf3 = kf3 \cdot cb \cdot cc^2$$

$$x = (cao - ca) / cao$$

$$V = V_0 - v_0 \cdot t$$

$$re = re2$$

$$rf = rf3$$

$$ra = -rd1 - 3 \cdot re2$$

$$rb = -2 \cdot rd1 - rf3$$

$$rc = rd1 + re2 - 2 \cdot rf3$$

$$rd = rd1 - 2 \cdot re2 + rf3$$

$$t_0 = 0, \quad t_f = 100$$

Initial value

1.5

2

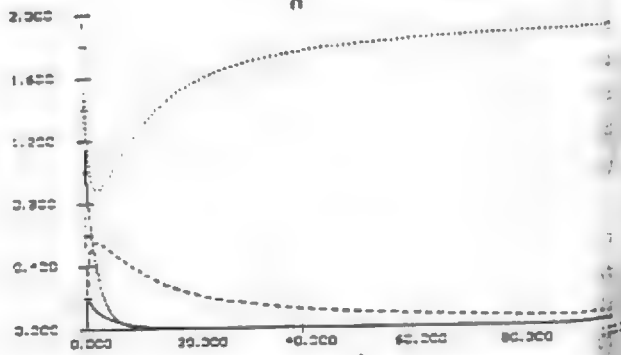
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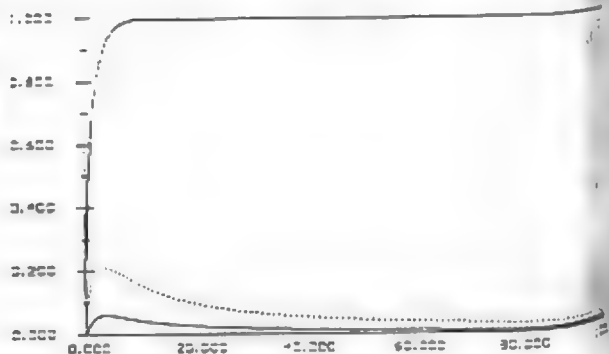
KEY:

— ca
... cb
— cc
-- cd



KEY:

— ce
... cf
— x



P6-13 cont'd

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	100	0	100
ca	1.5	1.5	7.61455e-36	7.61455e-36
cb	2	2	0.885955	1.89683
cc	0	0.185797	0	0.000270977
cd	0	0.553101	0	0.0513271
ce	0	0.0603835	0	0.00584598
cf	0	0.210084	0	0.0228647
co	10	10	10	10
cbo	2	2	2	2
cao	1.5	1.5	1.5	1.5
Vo	40	40	40	40
kd1	0.25	0.25	0.25	0.25
ke2	0.1	0.1	0.1	0.1
kf3	5	5	5	5
rd1	1.5	1.5	6.84919e-36	6.84919e-36
re2	0	0.038839	0	3.90832e-38
rf3	0	0.239239	0	6.96408e-07
x	0	1	0	1
v	40	1040	40	1040
re	0	0.038839	0	3.90832e-38
rf	0	0.239239	0	6.96408e-07
ra	-1.5	-6.96644e-36	-1.5	-6.96644e-36
rb	-3	-6.96408e-07	-3	-6.96408e-07
rc	1.5	1.5	-0.0276699	-1.39282e-06
rd	1.5	1.5	6.96408e-07	6.96408e-07

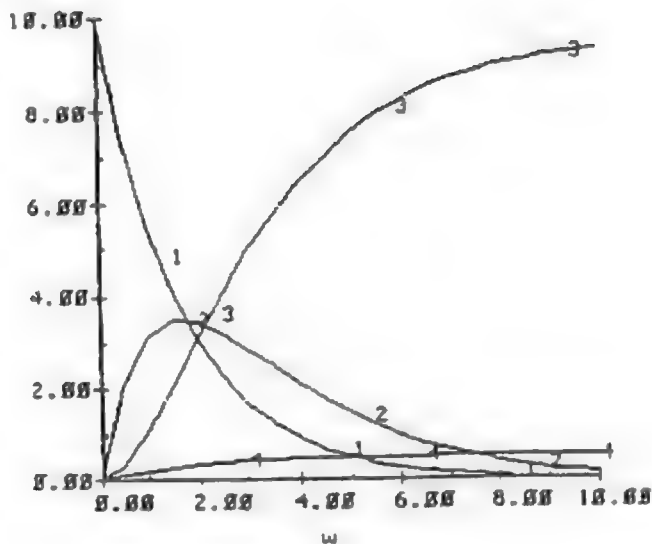
In case 1, A is the main species in the reactor after a good amount of time. In case 2, B is the main species after a time. The conversion of A is much greater in case 2 than in case 1. In case 1, however, E and F are formed more early on.

- d) When $\theta_B = 1$, the reaction does not form as much of any of the products. When $\theta_B = 10$, the conversion goes to 1 and a lot of F, but very little E are formed.

P6-14

$$\begin{aligned}
 v_0 C_{A0} - v_0 C_A + r_A W &= 0 & r_A &= -k_1 C_A - k_3 C_A \\
 -v_0 C_B + r_B W &= 0 & r_B &= k_1 C_A - k_2 C_B \\
 -v_0 C_C + r_C W &= 0 & r_C &= k_2 C_B \\
 -v_0 C_D + r_D W &= 0 & r_D &= k_3 C_A
 \end{aligned}$$

- KEY:
- 1 - ca
 - 2 - cb
 - 3 - cc
 - 4 - cd



P6-15

a) PFR
Mole balance:

$$\frac{dC_M}{d\tau} = r_M$$

$$\frac{dC_H}{d\tau} = r_H$$

$$\frac{dC_X}{d\tau} = r_X$$

$$\frac{dC_{Me}}{d\tau} = r_{Me}$$

$$\frac{dC_T}{d\tau} = r_T$$

$$\frac{dC_B}{d\tau} = r_B$$

Rate laws

$$r_M = -k_1 C_M C_H^{0.5}$$

$$r_H = r_M - k_2 C_X C_H^{0.5} - r_B$$

$$r_X = -r_M - k_2 C_X C_H^{0.5}$$

$$r_{Me} = -r_M + k_2 C_X C_H^{0.5} + r_B$$

$$r_T = k_2 C_X C_H^{0.5} - r_B$$

$$r_B = k_3 C_T C_H^{0.5}$$

$$C_{H0} = 0.021$$

$$C_{M0} = 0.0105$$

$$\tau = .5$$

Plugging those into POLYMATH gets the following:

6-34

P6-15 cont'd

CSTR:

Mole balance:

$$F_{H0} - F_H = (-r_{1H} - r_{2H} - r_{3H})V$$

$$F_{M0} - F_M = -r_{1M}V$$

$$F_X = (r_{1X} + r_{2X})V$$

$$F_T = (r_{2T} + r_{3T})V$$

$$F_{Me} = (r_{1Me} + r_{2Me} + r_{3Me})V$$

$$F_B = r_{3B}$$

Rate Law:

$$-r_{1M} = -r_{1H} = r_{1X} = r_{1Me} = k_1 C_H^{0.5} C_M$$

$$-r_{2H} = -r_{2X} = r_{2T} = r_{2Me} = k_2 C_H^{0.5} C_X$$

$$-r_{3H} = -r_{3T} = r_{3B} = r_{3Me} = k_3 C_H^{0.5} C_T$$

Stoichiometry:

$$F_H = v_0 C_H$$

$$F_M = v_0 C_M$$

$$F_X = v_0 C_X$$

$$F_T = v_0 C_T$$

$$F_{Me} = v_0 C_{Me} = v_0 (C_{H0} - C_H)$$

$$F_B = v_0 C_B = v_0 [(C_{M0} - C_M) - C_X - C_T]$$

Combining all of these:

$$C_{H0} - C_H = (k_1 C_H^{0.5} C_M + k_2 C_H^{0.5} C_X + k_3 C_H^{0.5} C_T)\tau$$

$$C_{M0} - C_M = k_1 C_H^{0.5} C_M \tau$$

$$C_X = (k_1 C_H^{0.5} C_M - k_2 C_H^{0.5} C_X)\tau$$

$$C_T = (k_2 C_X C_H^{0.5} - k_3 C_H^{0.5} C_X)\tau$$

$$C_{Me} = C_{H0} - C_H$$

$$C_B = (C_{M0} - C_M) - C_X - C_T$$

The following is the POLYMATH program and the summary table showing all of the concentrations.

Equations:

$$f(ch) = ch - cho + (k1 \cdot ch^{.5} \cdot cm - k2 \cdot ch^{.5} \cdot cx + k3 \cdot ct \cdot ch^{.5}) \cdot \tau au$$

$$f(cm) = cm - cmo + k1 \cdot ch^{.5} \cdot cm \cdot \tau au$$

$$f(cx) = (k1 \cdot ch^{.5} \cdot cm - k2 \cdot ch^{.5} \cdot cx) \cdot \tau au - cx$$

$$f(ct) = (k2 \cdot ch^{.5} \cdot cx - k3 \cdot ct \cdot ch^{.5}) \cdot \tau au - ct$$

$$cho = .021$$

$$k1 = 55.2$$

$$k2 = 30.2$$

$$k3 = 11.2$$

$$\tau au = .51$$

$$cmo = .0105$$

$$cme = cho - ch$$

$$cb = (cmo - cm) - cx - ct$$

Solution

Variable	Value	f()
ch	0.00776519	2.993e-15
cm	0.00301658	1.463e-14
cx	0.00317467	2.79e-14
ct	0.00286611	-1.495e-14
cho	0.021	
k1	55.2	
k2	30.2	
k3	11.2	
tau	0.51	
cmo	0.0105	
cme	0.0132348	
cb	0.0044264	

P6-15 cont'd

The conversion of Hydrogen and Mesitylene are then:

$$X_H = \frac{C_{H0} - C_H}{C_{H0}} = \frac{0.021 - 0.0078}{0.021} = 0.63$$

$$X_M = \frac{C_{M0} - C_M}{C_{M0}} = \frac{0.0105 - 0.0030}{0.0105} = .71$$

$$C_H = 0.0078 \text{ lb mol/ft}^3$$

$$C_T = 0.0029 \text{ lb mol/ft}^3$$

$$C_M = 0.0030 \text{ lb mol/ft}^3$$

$$C_{\text{---}} = 0.013 \text{ lb mol/ft}^3$$

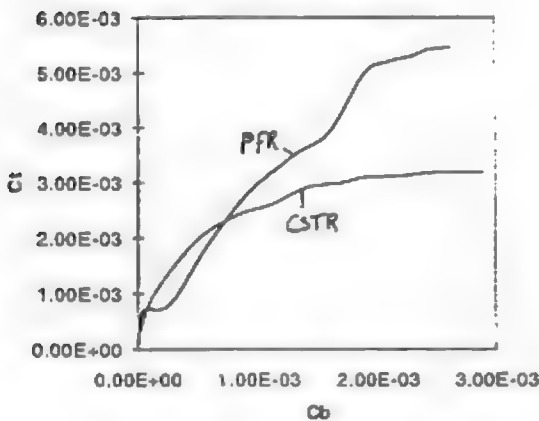
$$C_X = 0.0032 \text{ lb mol/ft}^3$$

$$C_B = 0.0014 \text{ lb mol/ft}^3$$

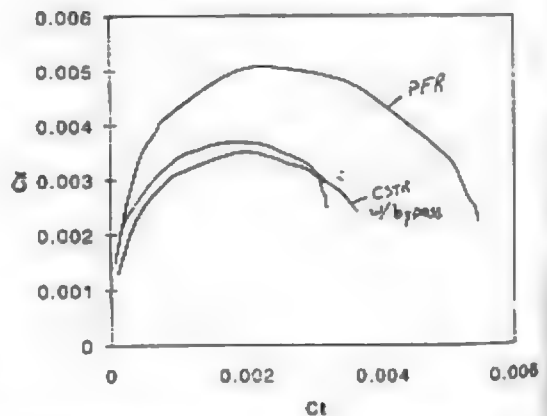
b) When θ_M is reduced to 1.5, it now takes a τ of 0.24 h to achieve a maximum of xylene. Increasing θ_M to 10 now requires a τ of only 0.08 h.

c) To find out the reactor schemes needed, use the attainable region theory to get these graphs:

Attainable region



Attainable region



Using a PFR would maximize C_X . If we used a ratio of mesitylene to hydrogen of 10, then we would only have to have a τ of .08 hours. So our volume of the reactor would be only 38.08 ft³. So our entering concentrations would be .0105 lb mol/ft³ of Hydrogen and .105 lb mol/ft³ of Mesitylene.

d) First find the proportionality constants of the rate constants using the Arrhenius equation.

$$k = A e^{-(E/RT)}$$

$$55.2 = A_1 e^{-(120000/(1.987 \cdot 833.3))}$$

$$A_1 = 9.72 \times 10^8$$

$$30.2 = A_2 e^{-(100000/(1.987 \cdot 833.3))}$$

$$A_2 = 12674$$

$$11.2 = A_3 e^{-(120000/(1.987 \cdot 833.3))}$$

$$A_3 = 8.28 \times 10^5$$

Once that is done, by trial and error come up with the temperature where $\bar{S}_{XT} = \bar{S}_{T0}$ and the answer is then 862K or 1551.6°R.

P6-15 cont'd

Equations:

$$d(cm)/d(t) = rm$$

$$d(ch)/d(t) = rh$$

$$d(cx)/d(t) = rx$$

$$d(cme)/d(t) = xme$$

$$d(ct)/d(t) = rt$$

$$d(cb)/d(t) = rb$$

$$rm = -55.2 \cdot cm \cdot ch^{.5}$$

$$rb = 11.2 \cdot ct \cdot ch^{.5}$$

$$rx = -rm - 30.2 \cdot cx \cdot ch^{.5}$$

$$rt = 30.2 \cdot cx \cdot ch^{.5} - rb$$

$$rh = rm - 30.2 \cdot cx \cdot ch^{.5} - rb$$

$$xme = -rm + 30.2 \cdot cx \cdot ch^{.5} + rb$$

$$t_0 = 0, \quad t_f = 0.51$$

Initial value

0.0105

0.021

0

0

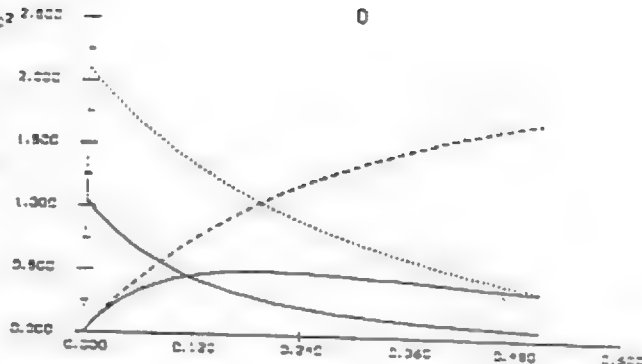
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Scale: 1.02 2.800

KEY:

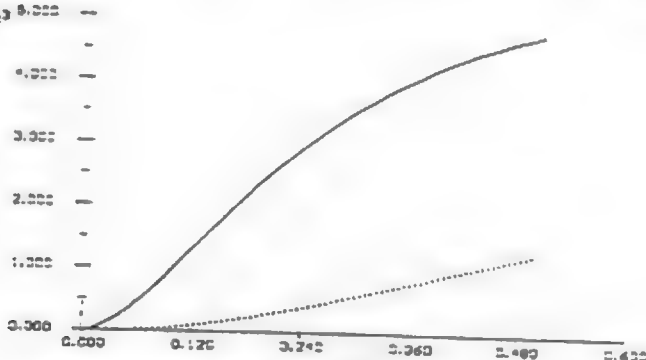
— cm
... ch
— cx
-- cme



Scale: 1.03 0.000

KEY:

— ct
... cb



Variable

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	0.51	0	0.51
cm	-0.0105	0.0105	0.000699836	0.000699836
ch	-0.021	0.021	0.00381847	0.00381847
cx	0	0.00506614	0	0.00372332
cme	0	0.0171815	0	0.0171815
ct	0	0.00477233	0	0.00477233
cb	0	0.00130452	0	0.00130452
rm	-0.083992	-0.00238715	-0.083992	-0.00238715
rb	0	0.00352127	0	0.00330288
rx	-0.083992	0.083992	-0.00523484	-0.0045612
rh	0	0.0146868	0	0.00364547
rt	-0.083992	-0.0126384	-0.083992	-0.0126384
xme	0.083992	0.083992	0.0126384	0.0126384

The maximum concentration of xylene occurs at $\tau = 0.19$ h.

P6-16

a)

Start with the mole balances:

$$\begin{aligned} \frac{dF_{11}}{dV} &= r_{11} & \frac{dF_{10}}{dV} &= r_{10} & \frac{dF_9}{dV} &= r_9 & \frac{dF_8}{dV} &= r_9 \\ \frac{dF_7}{dV} &= r_7 & \frac{dF_6}{dV} &= r_6 & \frac{dF_H}{dV} &= r_H \end{aligned}$$

Then the rate laws:

$$r_{11} = -k_1 C_H^5 C_{11}$$

$$r_{10} = k_1 C_H^5 C_{11} - k_2 C_H^5 C_{10}$$

$$r_9 = k_2 C_H^5 C_{10} - k_3 C_H^5 C_9$$

$$r_8 = k_3 C_H^5 C_9 - k_4 C_H^5 C_8$$

$$r_7 = k_4 C_H^5 C_8 - k_5 C_H^5 C_7$$

$$r_6 = k_5 C_H^5 C_7$$

$$r_H = k_1 C_H^5 C_{11} + k_2 C_H^5 C_{10} + k_3 C_H^5 C_9 + k_4 C_H^5 C_8 + k_5 C_H^5 C_7$$

Finally, the stoichiometry:

$$F = C \cdot v_0$$

Putting all of those together and put it into POLYMATH and get the following program and answers.

P6-16 Hydodealkylation ReactionsEquations:

$$d(c11)/d(V) = r1/v_0$$

$$d(c9)/d(V) = (-r2+r3)/v_0$$

$$d(c10)/d(V) = (-r1+r2)/v_0$$

$$d(c8)/d(V) = (-r3+r4)/v_0$$

$$d(c7)/d(V) = (-r4+r5)/v_0$$

$$d(c6)/d(V) = -r5/v_0$$

$$d(ch)/d(V) = (r1+r2+r3+r4+r5)/v_0$$

$$v_0 = 1$$

$$k5 = 2.1$$

$$s87 = c8 / (c7 + .0000001)$$

$$s89 = c8 / (c9 + .00001)$$

$$c110 = .1$$

$$s910 = c9 / (c10 + .00001)$$

$$s90 = c9 / (c10 + c8 + c7 + c6 + .00000001)$$

$$r5 = -k5 \cdot ch^{.5} \cdot c7$$

$$k1 = k5 \cdot 17.6$$

Initial value

0.137

0

0

0

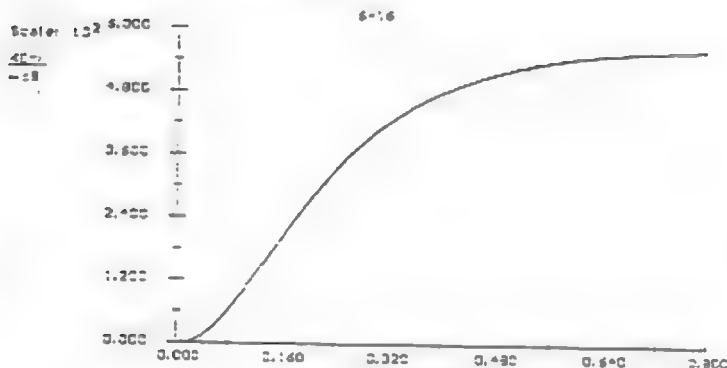
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0

0.389

P6-16 cont'd

$k2=k5 \cdot 10$
 $k3=k5 \cdot 4.4$
 $k4=k5 \cdot 2.7$
 $x=1-c11/c110$
 $z2=-k2 \cdot ch^{.5} \cdot c10$
 $z3=-k3 \cdot ch^{.5} \cdot c9$
 $r1=-k1 \cdot ch^{.5} \cdot c11$
 $r4=-k4 \cdot ch^{.5} \cdot c8$
 $V_0 = 0, \quad V_f = 10$



6-16

Variable	Initial value	Maximum value	Minimum value	Final value
V	0	0.800063	0	0.800063
c9	0	0.0661357	0	0.0452049
c11	0.137	0.137	0.000109711	0.000109711
c10	0	0.0651101	0	0.00526749
c8	0	0.0560404	0	0.0560404
c7	0	0.0270125	0	0.0270125
c6	0	0.00336495	0	0.00336495
ch	0.389	0.389	0.000326609	0.000326609
vo	1	1	1	1
k5	2.1	2.1	2.1	2.1
S87	0	84.4133	0	2.0746
s89	0	1.23942	0	1.23942
c110	0.1	0.1	0.1	0.1
s910	0	0.56561	0	8.56561
s90	0	0.978962	0	0.493044
z5	-0	-0	-0.00709141	-0.00102518

P6-16 cont'd

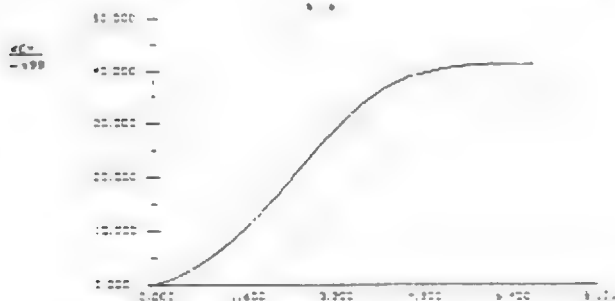
k1	36.96	36.96	36.96	36.96
k2	21	21	21	21
k3	9.24	9.24	9.24	9.24
k4	5.67	5.67	5.67	5.67
x	-0.37	0.998903	-0.37	0.998903
r1	-3.15811	-7.32818e-05	-3.15811	-7.32818e-05
r2	-0	-0	-0.697704	-0.00199911
r3	-0	-0	-0.220371	-0.00754869
r4	-0	-0	-0.0623892	-0.00574247

The ratio of hydrogen to pentamethylbenzene is 2.83 and the volume is 0.8 m³.

b) Shown in this POLYMATH program, which is the same as the first, we see that the ratio now becomes 4.8 to 1 and the volume increases to 6.8 m³ to maximize S₉₉. To maximize S₉₉ it follows that the volume would be smaller because the earlier the reaction is ended the less C7 that is formed.

6-16

Variable	Initial value	Maximum value	Minimum value	Final value
V	0	6.88499	0	6.88499
c5	0	0.0444059	0	1.59259e-05
c11	0.092	0.092	2.56915e-18	2.56915e-18
c18	0	0.0437213	0	8.37446e-11
c8	0	0.0387026	0	0.00107129
c7	0	0.0464547	0	0.0238096
c6	0	0.0671031	0	0.0671031
ch	0.434	0.434	3.29003e-11	3.29003e-11
vo	1	1	1	1
k5	2.1	2.1	2.1	2.1
S87	0	75.7226	0	0.0449937
S89	0	41.3212	0	41.3212
c110	0.1	0.1	0.1	0.1
S910	0	136.668	0	1.59258
S95	0	0.978912	0	0.000173138
r5	-0	-0	-0.0272308	-2.86795e-37
k1	36.96	36.96	36.96	36.96
k2	21	21	21	21
k3	9.24	9.24	9.24	9.24
k4	5.67	5.67	5.67	5.67
x	0.08	1	0.08	1
r1	-2.24009	-5.44655e-22	-2.24009	-5.44655e-22
r2	-0	-0	-0.538785	-1.00873e-14
r3	-0	-0	-0.204868	-8.44065e-10
r4	-0	-0	-0.0887499	-3.42409e-08



- (a) Enter the given program into POLYMATH. Equations for the concentrations must be added.

The following maximums can be seen in the graph given. (More exact values can be found in the corresponding table in POLYMATH.)

$$C_{\text{Cmax}} = 0.0434 \quad \text{and} \quad C_{\text{Dmax}} = 0.0033$$

Equations:

	Initial value
$d(fc)/d(v) = k1 \cdot (fa/ft) \cdot (fb/ft) \cdot (1/2) - k3 \cdot (fc/ft) + k4 \cdot (fw/ft) \cdot (fd/ft)$	0
$d(fa)/d(v) = -k1 \cdot (fa/ft) \cdot (fb/ft) \cdot (1/2) - k2 \cdot (fa/ft) \cdot (fb/ft)$	9.83
$d(fb)/d(v) = -k1/2 \cdot (fa/ft) \cdot (fb/ft) \cdot (1/2)$	4.91
$d(fw)/d(v) = k3 \cdot (fc/ft) - k4 \cdot (fw/ft) \cdot (fd/ft)$	0
$d(fd)/d(v) = k2/2 \cdot (fa/ft) \cdot (fb/ft) - k4 \cdot (fd/ft) \cdot (fw/ft)$	0
$d(fe)/d(v) = k3 \cdot (fc/ft)$	0
$d(fg)/d(v) = k4 \cdot (fw/ft) \cdot (fd/ft)$	0

$$k1 = 0.04$$

$$ft = fa + fb + fc + fd + fe + fw + fg$$

$$k2 = 0.007$$

$$k3 = 0.014$$

$$k4 = 0.45$$

$$v_0 = 100$$

$$cto = 0.147$$

$$ca = cto \cdot (fa/ft)$$

$$cb = cto \cdot (fb/ft)$$

$$cc = cto \cdot (fc/ft)$$

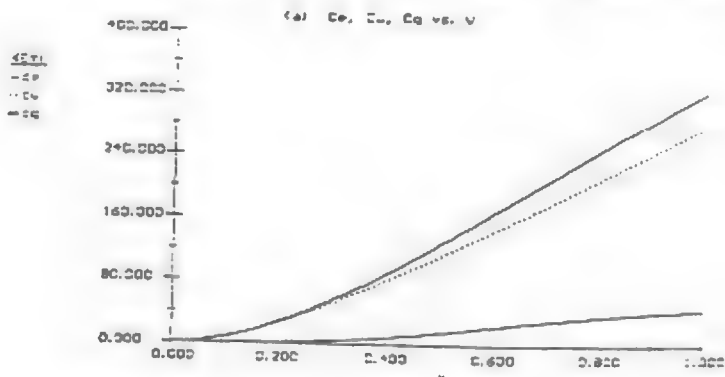
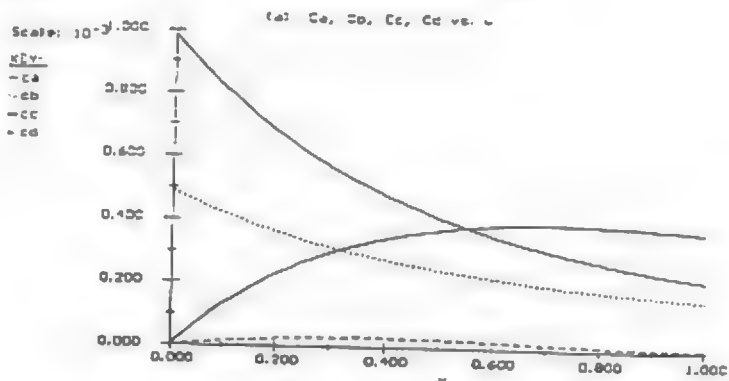
$$cd = cto \cdot (fd/ft)$$

$$ce = cto \cdot (fe/ft)$$

$$cw = cto \cdot (fw/ft)$$

$$cg = cto \cdot (fg/ft)$$

$$v_0 = 0, \quad v_f = 1000$$



(b)

$$\text{Overall yield of HCOOH: } \bar{Y}_c = \frac{F_c}{F_{A0} - F_A}$$

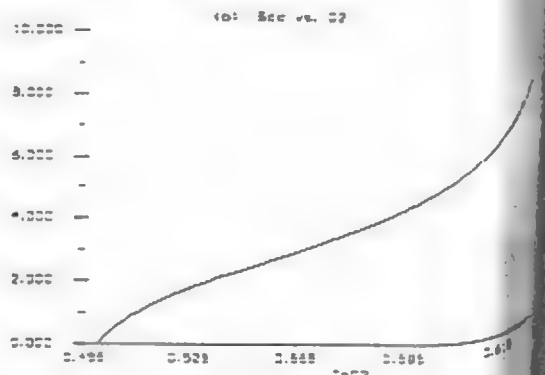
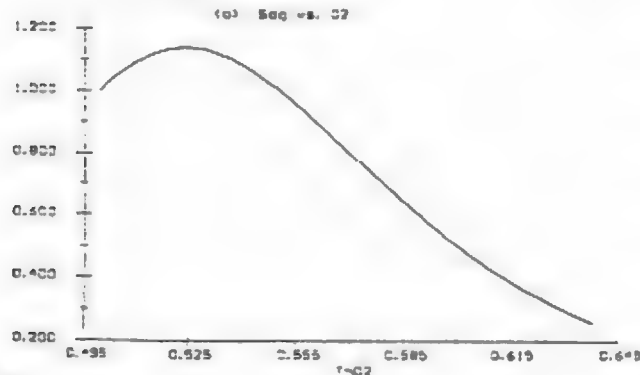
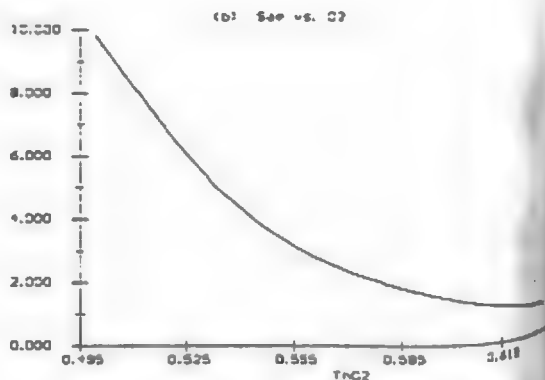
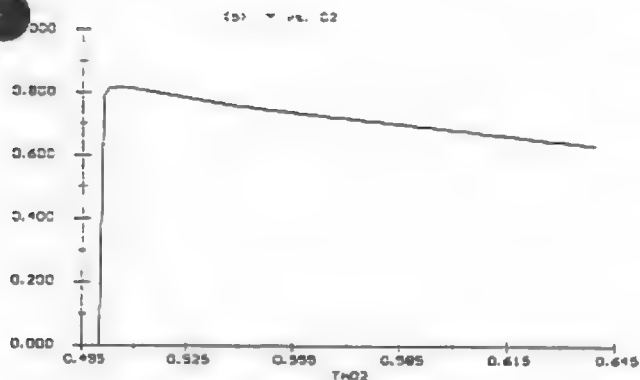
$$\text{Selectivity of HCHO to CO: } \tilde{S}_{AE} = \frac{F_A}{F_E}$$

$$\text{Selectivity of HCOOCH}_3 \text{ to CH}_3\text{OH: } \tilde{S}_{DG} = \frac{F_D}{F_G}$$

$$\text{Selectivity of HCOOH to HCOOCH}_3: \tilde{S}_{CD} = \frac{F_C}{F_D}$$

$$\Theta_{O_2} = \frac{C_B}{C_A}$$

Add these equations to the previous program and use it to generate the desired plots.



- (c) Modify the original POLYMATH program by adding y to each of the concentration terms. Also add the following equation:

$$\frac{dy}{dV} = \frac{-\alpha}{2y} \left(\frac{F_T}{F_{T_0}} \right)$$

$$\alpha = 0.002 \quad F_{T_0} = 15$$

The graphs of concentration down the reactor are very similar to those generated in part (a). The only major difference is that with the change in pressure, the maximum reactor volume is significantly smaller.

Equations:

	<u>Initial value</u>
$d(f_c)/d(v) = k_1 \cdot (f_a/f_t) \cdot (f_b/f_t) \cdot (1/2) \cdot y - k_3 \cdot (f_c/f_t) \cdot y + k_4 \cdot (f_w/f_t) \cdot (f_d/f_t) \cdot y$	0
$d(f_a)/d(v) = -k_1 \cdot (f_a/f_t) \cdot (f_b/f_t) \cdot (1/2) \cdot y - k_2 \cdot (f_a/f_t) \cdot (1/2) \cdot y$	10
$d(f_b)/d(v) = -k_1/2 \cdot (f_a/f_t) \cdot (f_b/f_t) \cdot (1/2) \cdot y$	5
$d(f_w)/d(v) = k_3 \cdot (f_c/f_t) \cdot y - k_4 \cdot (f_w/f_t) \cdot (f_d/f_t) \cdot y$	0
$d(f_d)/d(v) = k_2/2 \cdot (f_a/f_t) \cdot (1/2) \cdot y - k_4 \cdot (f_w/f_t) \cdot (f_d/f_t) \cdot y$	0
$d(f_e)/d(v) = k_3 \cdot (f_c/f_t) \cdot y$	0
$d(f_g)/d(v) = k_4 \cdot (f_w/f_t) \cdot (f_d/f_t) \cdot y$	0
$d(y)/d(v) = -0.002/2 \cdot y \cdot (f_t/f_{t_0})$	1

$$k_2 = 0.007$$

$$k_1 = 0.04$$

$$f_t = f_a + f_b + f_c + f_d + f_e + f_w + f_g$$

$$k_3 = 0.014$$

$$k_4 = 0.45$$

$$v_0 = 100$$

$$f_{t_0} = 15$$

$$c_a = f_a/v_0$$

$$c_b = f_b/v_0$$

$$c_c = f_c/v_0$$

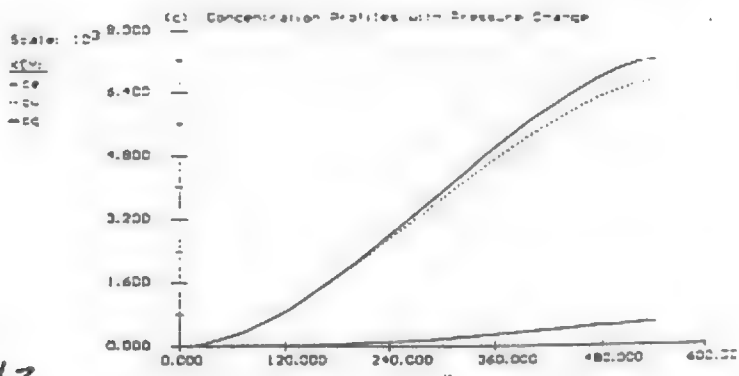
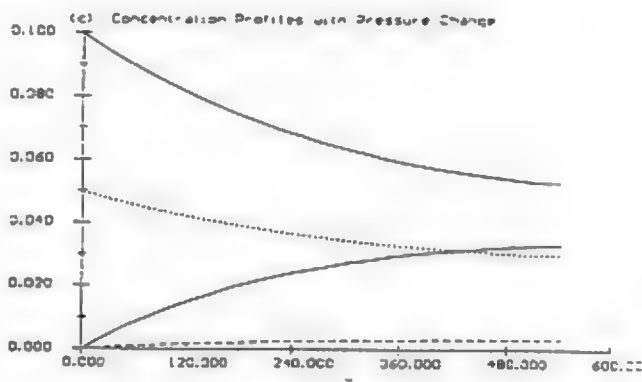
$$c_d = f_d/v_0$$

$$c_e = f_e/v_0$$

$$c_w = f_w/v_0$$

$$c_g = f_g/v_0$$

$$v_0 = 0, \quad v_f = 1000$$



P6-17 (cont'd)

(d)

$$k_{i,1} = k_{i,\infty} \exp\left(\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_\infty}\right)\right)$$

Substitute this equation in for all of the k values. Vary T and find out what temperature maximizes the yield of C .

The best temperature at which to run the reactor is 523 K or 250°C.

P6-18

(a)

Mole Balances: $\frac{dF_C}{dV} = r_C$ $\frac{dF_P}{dV} = r_P$ $\frac{dF_A}{dV} = r_A$ $\frac{dF_O}{dV} = r_O$

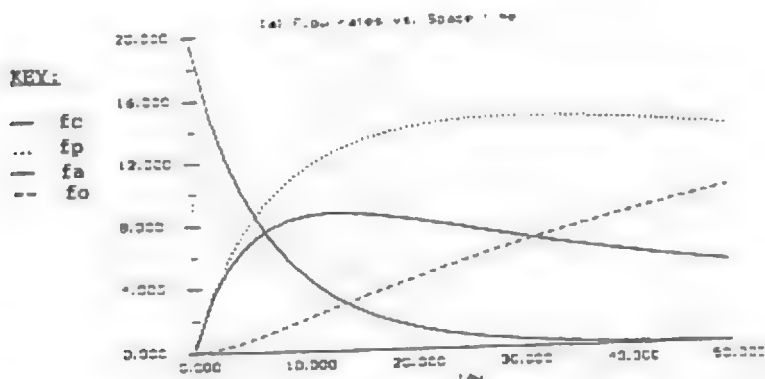
Rate Laws: $r_C = -k_1 C_C - k_2 C_C$ $r_P = k_1 C_C - k_3 C_P + k_4 C_A$

$r_A = k_1 C_C + k_3 C_P - k_4 C_A - k_5 C_A$ $r_O = k_5 C_A$

Stoichiometry: $C_C = C_{T0} \left(\frac{F_C}{F_T}\right)$ $C_P = C_{T0} \left(\frac{F_P}{F_T}\right)$ $C_A = C_{T0} \left(\frac{F_A}{F_T}\right)$ $C_O = C_{T0} \left(\frac{F_O}{F_T}\right)$

$F_T = F_C + F_P + F_A + F_O$

Use these equations in POLYMATH to generate a plot of the flow rates vs. τ .



(b) For a CSTR

Mole Balances: $F_C = F_{C0} + r_C V$ $F_P = r_P V$ $F_A = r_A V$ $F_O = r_O V$

Rate Laws: $r_C = -k_1 C_C - k_2 C_C$ $r_P = k_1 C_C - k_3 C_P + k_4 C_A$

$r_A = k_1 C_C + k_3 C_P - k_4 C_A - k_5 C_A$ $r_O = k_5 C_A$

6-44

P6-18 (cont'd)

Stoichiometry: $F_C = v_o C_C$ $F_P = v_o C_P$ $F_A = v_o C_A$ $F_O = v_o C_O$

Combine: $f(C_C) = 0 = C_C - C_{C0} + (k_1 + k_2) C_C \tau$
 $f(C_P) = 0 = C_P - (k_1 C_C - k_3 C_P + k_4 C_A) \tau$
 $f(C_A) = 0 = C_A - (k_1 C_C - k_3 C_P - k_4 C_A - k_5 C_A) \tau$
 $f(C_O) = 0 = C_O - k_5 C_A \tau$

Use these equations in POLYMATH to generate values for the flow rates at different values of τ . Use these values to generate the desired curve.

Equations:

$f(cc) = cc - cco + (k1 + k2) * cc * \tau$
 $f(cp) = cp - (k1 * cc - k3 * cp + k4 * ca) * \tau$
 $f(ca) = ca - (k1 * cc - k3 * cp - k4 * ca - k5 * ca) * \tau$
 $f(co) = co - k5 * ca * \tau$

Initial value

2
0
0
0

$cco = 2$

$k1 = 0.12$

$k2 = 0.046$

$k3 = 0.02$

$k4 = 0.034$

$vo = 10$

$k5 = 0.04$

$V = 3000$

$fc = vo * cc$

$fp = vo * cp$

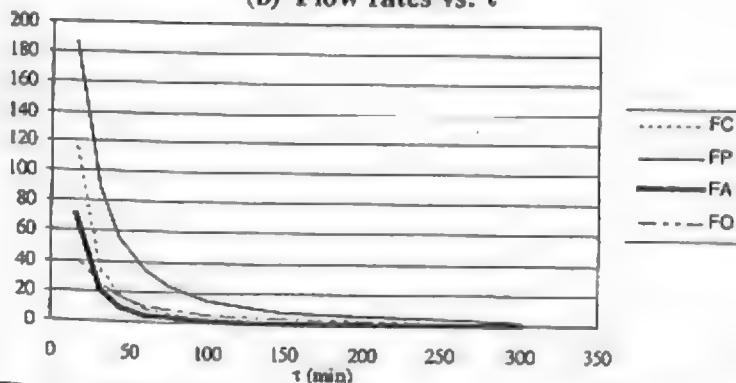
$fa = vo * ca$

$fo = vo * co$

$\tau = V / vo$

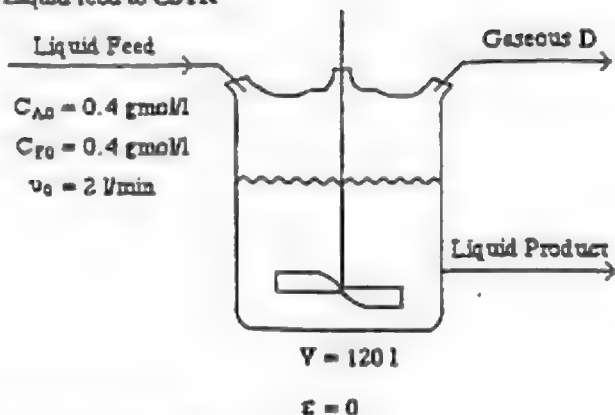
Variable	Solution	
	Value	f()
cc	0.0393701	-8.945e-17
cp	0.211711	-1.078e-16
ca	0.00633865	-2.309e-15
co	0.0760638	-8.518e-18
cco	2	
k1	0.12	
k2	0.046	
k3	0.02	
k4	0.034	
vo	10	
k5	0.04	
V	3000	
fc	0.393701	
fp	2.11711	
fa	0.0633865	
fo	0.760638	
tau	300	

(b) Flow rates vs. τ

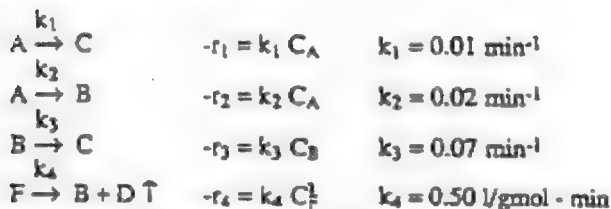


6-45

Given: Liquid feed to CSTR



With the following reaction sequence



(a) Since C is an end product, formed through intermediate B by either $A \xrightarrow{k_2} B \xrightarrow{k_3} C$ or $F \xrightarrow{k_4} B + D \uparrow \xrightarrow{k_3} C$, or directly from $A \xrightarrow{k_1} C$, the maximum concentration of C occurs when all A and F have been converted to C: $C_{\max} = C_{A0} + C_{F0}$, (with $\epsilon = 0$).

(b) Both A and F are only decomposed by the above scheme:

Balance on A: $v_0 C_{A0} - v_0 C_A = (-r_A) V = (-r_1 - r_2) V = (k_1 + k_2) C_A V \quad (a)$

$$\frac{C_{A0} - C_A}{C_A} = (k_1 + k_2) \frac{V}{v_0} = (k_1 + k_2) \tau$$

$$\text{or } C_A = \frac{C_{A0}}{1 + (k_1 + k_2) \tau} = \frac{0.4 \text{ gmol/l}}{1 + (0.01 + 0.02) \text{ min}^{-1} \left(\frac{120 \text{ l}}{2 \text{ l/min}} \right)} = \frac{0.4 \text{ gmol/l}}{1 + (0.03) (60)}$$

$$C_A = 0.143 \text{ gmol/l}$$

Balance on F: $v_0 C_{F0} - v_0 C_F = (-r_F) V = k_4 C_F^2 V \quad (b)$

$$k_4 \tau C_F^2 + C_F - C_{F0} = 0 \quad \text{where } \tau = \frac{V}{v_0} = 60 \text{ min}$$

Rate Laws:

$$\begin{aligned} -r_A &= r_{1A} + r_{2A} + 2/3 r_{4C} & -r_B &= 1.25 r_{1A} + 0.75 r_{2A} + r_{3B} \\ -r_C &= -r_{1A} + 2 r_{3B} + r_{4C} & -r_D &= -1.5 r_{1A} - 1.5 r_{2A} - r_{4C} \\ -r_E &= -0.5 r_{2A} - 5/6 r_{4C} & -r_F &= -2 r_{3B} \end{aligned}$$

Use these equations in POLYMATH to find the exiting molar flow rates.

Equations:

$$\begin{aligned} f(a) &= v_0 \cdot c_a - f_{ao} - r_a \cdot W \\ f(b) &= v_0 \cdot c_b - f_{bo} - r_b \cdot W \\ f(c) &= v_0 \cdot c_c - r_c \cdot W \\ f(d) &= v_0 \cdot c_d - r_d \cdot W \\ f(e) &= v_0 \cdot c_e - r_e \cdot W \\ f(f) &= v_0 \cdot c_f - r_f \cdot W \end{aligned}$$

$$\begin{aligned} v_0 &= 10 \\ f_{ao} &= 10 \\ c_a &= 1 \\ f_{bo} &= 10 \\ v_0 &= 0.0012 \\ r_1 &= k_1 \\ r_2 &= k_2 \\ r_3 &= k_3 \\ r_4 &= k_4 \end{aligned}$$

$$\begin{aligned} f_a &= v_0 \cdot c_a \\ f_b &= v_0 \cdot c_b \\ f_c &= v_0 \cdot c_c \\ f_d &= v_0 \cdot c_d \\ f_e &= v_0 \cdot c_e \\ f_f &= v_0 \cdot c_f \end{aligned}$$

$$\begin{aligned} r_1 &= k_1 \cdot c_a \cdot c_b^{0.2} \\ r_2 &= k_2 \cdot c_a \cdot c_b \\ r_3 &= k_3 \cdot c_c \cdot c_a^{(2/3)} \\ r_4 &= k_4 \cdot c_c^{0.2} \cdot c_b \end{aligned}$$

$$\begin{aligned} r_e &= 0.5 \cdot r_2 + (5/6) \cdot r_4 \\ r_a &= -r_1 + r_2 - (2/3) \cdot r_4 \\ r_b &= -1.25 \cdot r_1 - 0.75 \cdot r_2 - r_3 \\ r_c &= r_1 - 2 \cdot r_3 - r_4 \\ r_d &= 1.5 \cdot r_1 + 1.5 \cdot r_2 - r_4 \end{aligned}$$

Initial value

$$\begin{aligned} 1 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{aligned}$$

Variable	Value	f(1)	Variable	Value	f(2)
ca	0.998927	-3.912e-16	fe	0.00361292	
cb	0.997227	6.28e-16	ff	2.2874e-07	
cc	0.00178488	-1.574e-16	ra	0.00596037	
cd	0.00376122	-7.373e-17	rb	0.00239078	
ce	0.000361292	6.614e-18	rc	1.07016e-05	
cf	2.2874e-08	-9.264e-19	rd	1.91234e-08	
vo	10		re	7.52458e-08	
fao	10		rf	0.00120431	
u	3		ra	-0.00357672	
fbo	10		rb	-0.00824358	
v_0	0.0012		rc	0.00596037	
k1	5		rd	0.0125374	
k2	2				
k3	10				
k4	5				
ra	9.98927				
rb	9.97227				
rc	0.0178488				
rd	0.0376122				

$$\begin{aligned} r_1 &= r_{ho} \cdot k_1 \cdot c_a \cdot c_b^{0.2} \\ r_2 &= r_{ho} \cdot k_2 \cdot c_a \cdot c_b \\ r_3 &= r_{ho} \cdot k_3 \cdot c_c \cdot c_a^{(2/3)} \\ r_4 &= r_{ho} \cdot k_4 \cdot c_c^{0.2} \cdot c_b \end{aligned}$$

$$\bar{Y}_{AE} = \frac{F_E}{F_{Ao} - F_A} = \frac{3.6 \times 10^{-3}}{10 - 9.989} = 0.336$$

$$\bar{Y}_{BF} = \frac{F_F}{F_{Bo} - F_B} = \frac{2.29 \times 10^{-7}}{10 - 9.973} = 8.25 \times 10^{-6}$$

$$\bar{Y}_{AC} = \frac{F_C}{F_{Ao} - F_A} = \frac{0.0178}{10 - 9.989} = 1.663$$

6-47

P6-23 cont'd

Equations:

$$f(fh) = (-rh) \cdot V - fho - fh$$

$$f(fc) = rc \cdot V - fc$$

$$f(fca) = rca \cdot V - fca$$

$$V = 1000$$

$$fho = 10000$$

$$fb = 4320$$

$$fbo = 7200$$

$$k1 = 2.7$$

$$K1 = 0.0264$$

$$k2 = 0.07$$

$$K2 = 0.04$$

$$T = 403$$

$$Pbo = 1400$$

$$R = 8.309$$

$$Pb = Pbo \cdot .6$$

$$vo = 2.41e7 / Pbo$$

$$Ph = fh \cdot 8.309 \cdot 403 / vo$$

$$y = fc / (fbo - fb)$$

$$Pc = fc \cdot 8.309 \cdot T / vo$$

$$Pho = fho \cdot R \cdot T / vo$$

$$rb = (k1 \cdot K1 \cdot Pb \cdot Ph \cdot .5) / (1 + K1 \cdot Pb)$$

$$rca = k2 \cdot K2 \cdot Pc \cdot Ph / (1 + K2 \cdot Pc)$$

$$rh = (rb) - k2 \cdot K2 \cdot Pc \cdot Ph / (1 + K2 \cdot Pc)$$

$$rc = - (rb) - k2 \cdot K2 \cdot Pc \cdot Ph / (1 + K2 \cdot Pc)$$

Initial value

$$1e-09$$

$$8$$

$$0.5$$

Solution

Variable	Value	f()	Variable	Value	f()
fh	63.5619	5.826e-13	Pho	1945.2	
fc	8232.08	1.847e-12	rb	-9.08426	
fca	852.181	2.842e-14	rca	0.852181	
V	1000		rh	-9.93644	
fho	10000		rc	8.23208	
fb	4320				
fbo	7200				
k1	2.7				
K1	0.0264				
k2	0.07				
K2	0.04				
T	403				
Pbo	1400				
R	8.309				
Pb	840				
vo	17214.3				
Ph	12.3641				
y	2.85836				
Pc	1601.31				

The highest yield occurs at pressures: $P_{BO} = 1400 \text{ kPa}$
 $P_{HO} = 1945.2 \text{ kPa}$

P6-24

(a)

Mole Balances:

$$\begin{aligned}\frac{dF_A}{dV} &= r_{1A} + r_{2A} & \frac{dF_B}{dV} &= 2r_{1A} - r_{2A} - r_{3C} & \frac{dF_C}{dV} &= -r_{1A} + r_{3C} \\ \frac{dF_D}{dV} &= r_{2A} & \frac{dF_E}{dV} &= -r_{2A} & \frac{dF_G}{dV} &= -r_{3C}\end{aligned}$$

Rate Laws:

$$\begin{aligned}-r_{1A} &= k_1(C_A C_B^2 - C_C/K_1) \\ -r_{2A} &= k_2(C_A C_D - C_E C_B/K_2) \\ -r_{3C} &= k_3 C_C\end{aligned}$$

Stoichiometry:

$$C_i = C_{T0} \left(\frac{F_i}{F_T} \right) \left(\frac{T_2}{T} \right)$$

$$F_T = F_A + F_B + F_C + F_D + F_E + F_G$$

$$C_{T0} = \frac{P_0}{RT_0}$$

Use these equations in POLYMATH. Vary P_0 and T_0 to find the optimal conditions. We determine these to be:

$$T_0 = 315.8 \text{ K} \quad P_0 = 160 \text{ atm} \quad V = 100 \text{ dm}^3$$

6-24

Equations:

$$\begin{aligned}d(fa)/d(v) &= -r_{2a} \\ d(fb)/d(v) &= 2 \cdot r_{1a} - r_{2a} - r_{3c} \\ d(fa)/d(v) &= r_{1a} + r_{2a} \\ d(fc)/d(v) &= -r_{1a} - r_{3c} \\ d(fg)/d(v) &= -r_{3c} \\ d(fd)/d(v) &= r_{2a} \\ ft &= fa + fb + fc + fd + fe + fg\end{aligned}$$

$$T_0 = 315.8$$

$$P_0 = 160$$

$$T = T_0$$

$$k_1 = .933 \cdot \exp(12.5 \cdot (31400/1.987 \cdot (1/330 - 1/T)))$$

$$K_1 = 131667 \cdot (0.00198 \cdot T)^{-2} \cdot \exp(30620/1.987 \cdot (1/T - 1/298))$$

$$k_2 = .636 \cdot \exp(18000/1.987 \cdot (1/300 - 1/T))$$

$$K_2 = 103943 \cdot \exp(19834/1.987 \cdot (1/T - 1/298))$$

$$k_3 = .244 \cdot \exp(1.5 \cdot 28956/1.987 \cdot (1/325 - 1/T))$$

$$C_{T0} = P_0 / (1.082 \cdot T_0)$$

$$ca = C_{T0} \cdot (fa/ft) \cdot (T_0/T)$$

$$cb = C_{T0} \cdot (fb/ft) \cdot (T_0/T)$$

$$cc = C_{T0} \cdot (fc/ft) \cdot (T_0/T)$$

$$cd = C_{T0} \cdot (fd/ft) \cdot (T_0/T)$$

$$ce = C_{T0} \cdot (fe/ft) \cdot (T_0/T)$$

$$r_{3c} = k_3 \cdot cc$$

$$r_{1a} = -k_1 \cdot (ca \cdot cb^2 - cc/K_1)$$

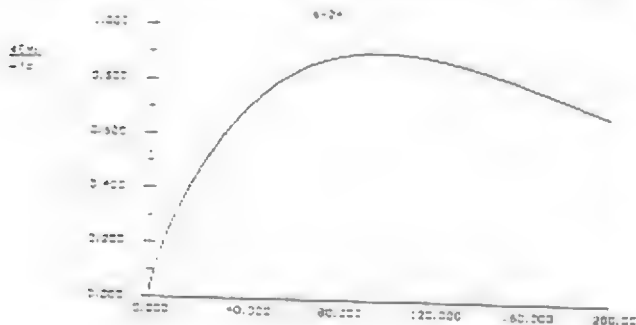
$$r_{2a} = -k_2 \cdot (ca \cdot cd - ce/K_2)$$

$$v_0 = 0, \quad v_2 = 200$$

P6-24 (cont'd)

6-24

Variable	Initial value	Maximum value	Minimum value	Final value
v	0	200	0	200
fe	6	9.99892	6	9.99558
fb	14	17.3038	14	15.4939
fa	6	6	0.184792	0.184792
fc	0	0.907053	0	0.682081
fg	0	1.13754	0	1.13754
fd	4	4	0.0010827	0.00441766
ft	30	30	27.4837	27.4983
To	315.8	315.8	315.8	315.8
Po	160	160	160	160
T	315.8	315.8	315.8	315.8
k1	0.00428571	0.00428571	0.00428571	0.00428571
K1	2791.12	2791.12	2791.12	2791.12
K2	2.88122	2.88122	2.88122	2.88122
K2	40761.5	40761.5	40761.5	40761.5
k3	0.0343899	0.0343899	0.0343899	0.0343899
Cto	6.17866	6.17866	6.17866	6.17866
ca	1.23573	1.23573	0.0415214	0.0415214
cb	2.88337	3.61472	2.88337	3.48136
cc	0	0.202498	0	0.153258
cd	0.823821	0.823821	0.00236662	0.000992615
ce	1.23573	2.24735	1.23573	2.24593
r3c	-0	-0	-0.00696389	-0.00527054
r1a	-0.0440299	-0.00215647	-0.0440299	-0.00215647
r2a	-2.93305	4.00241e-05	-2.93305	4.00043e-05



Methanol Synthesis

v	Yc
0	0
20	0.44820445
40	0.68570232
60	0.82334782
80	0.8904273
100	0.90829749
120	0.89276842
140	0.85543262
160	0.80470055
180	0.74660073
200	0.6853895

- (b) Use the same POLYMATH program as above and vary the ratio of entering reactants. The optimal ratio would be :

$\frac{1}{13}$ hydrogen gas, $\frac{4}{13}$ carbon monoxide, and $\frac{1}{3}$ carbon dioxide

These results are similar to those in part (a) in that the optimal volume is still 100 dm³, and the concentration profile is very similar in shape. The primary difference is that the F_c values are more than doubled.

Methanol Synthesis

Equations:

$$r_a(F_a)/d(V) = r_{1a} + r_{2a}$$

$$r_b(F_b)/d(V) = 2 \cdot r_{1a} - r_{2a} - r_{3c}$$

$$r_c(F_c)/d(V) = -r_{1a} + r_{3c}$$

$$r_d(F_d)/d(V) = -r_{2a}$$

$$r_e(F_e)/d(V) = -r_{3c}$$

$$r_f(F_d)/d(V) = r_{2a}$$

$$F_t = F_a + F_b + F_c + F_d + F_e + F_g$$

$$T_0 = 315.8$$

$$P_0 = 160$$

$$T = T_0$$

$$k_1 = .933 \cdot \exp((2.5 \cdot (31400/1.987 \cdot (1/330 - 1/T)))$$

$$k_1 = 131667 \cdot (0.00198 \cdot T)^2 \cdot \exp(30620/1.987 \cdot (1/T - 1/298))$$

$$k_2 = 0.636 \cdot \exp(18000/1.987 \cdot (1/300 - 1/T))$$

$$k_3 = 103943 \cdot \exp(9834/1.987 \cdot (1/T - 1/298))$$

$$k_4 = 0.244 \cdot \exp(1.5 \cdot 28956/1.987 \cdot (1/325 - 1/T))$$

$$C_{to} = P_0 / (.082 \cdot T_0)$$

$$C_a = C_{to} \cdot (F_a/F_t) \cdot (T_0/T)$$

$$C_b = C_{to} \cdot (F_b/F_t) \cdot (T_0/T)$$

$$C_c = C_{to} \cdot (F_c/F_t) \cdot (T_0/T)$$

$$C_d = C_{to} \cdot (F_d/F_t) \cdot (T_0/T)$$

$$C_e = C_{to} \cdot (F_e/F_t) \cdot (T_0/T)$$

$$r_{3c} = -k_3 \cdot C_c$$

$$r_{1a} = -k_1 \cdot (C_a \cdot C_b^2 - C_c / K_1)$$

$$r_{2a} = -k_2 \cdot (C_a \cdot C_d - C_e \cdot C_b / K_2)$$

$$V_0 = 0, \quad V_f = 200$$

Methanol Synthesis

V	Fc
20	0
40	1.2448568
60	2.0129151
80	2.4406221
100	2.6366715
120	2.680932
140	2.6292203
160	2.5193659
180	2.376518
200	2.2171669
	2.0519865

Initial value

8

16

0

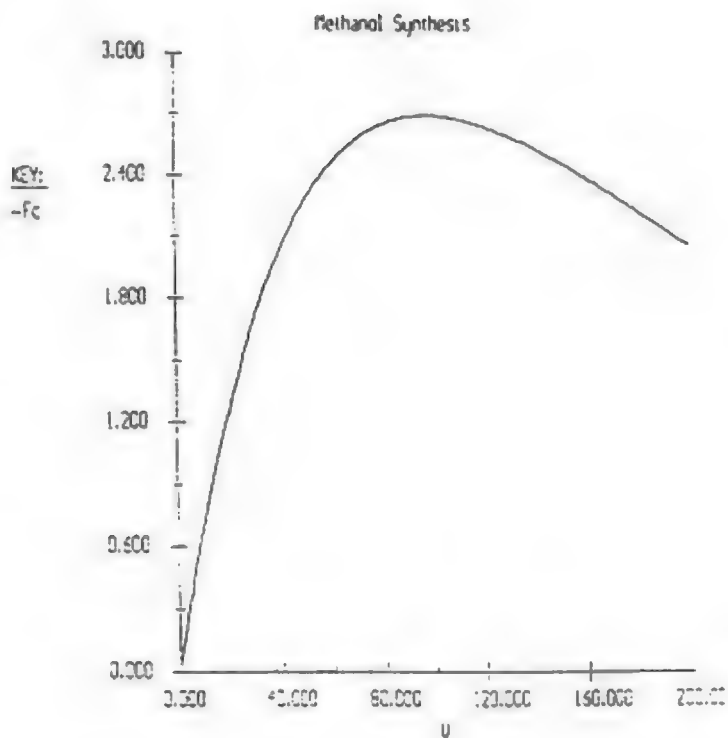
6

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0

Methanol Synthesis

Variable	Initial value	Maximum value	Minimum value	Final value
a	0	200	0	200
b	8	8	1.94105	1.94105
c	16	16	7.88788	7.88788
d	0	2.6816	0	2.05199
e	6	6	5.99941	5.99941
f	0	4.00756	0	4.00756
g	0	0.000590838	0	0.000590838
t	30	30	21.8885	21.8885
to	315.8	315.8	315.8	315.8
po	160	160	160	160
t	315.8	315.8	315.8	315.8
k1	0.00428571	0.00428571	0.00428571	0.00428571
k2	2791.12	2791.12	2791.12	2791.12
k3	2.88122	2.88122	2.88122	2.88122
k4	40761.5	40761.5	40761.5	40761.5
k5	0.3143899	0.3143899	0.3143899	0.3143899
cto	6.17866	6.17866	6.17866	6.17866
ca	1.64764	1.64764	0.547917	0.547917
cb	3.29528	3.29528	2.22658	2.22658
cd	0	0.724399	0	0.579211
ce	0	0.000166781	0	0.000166781
rc	1.21373	1.69351	1.23573	1.69351
ria	-0	-0	-0.024912	-0.024912
r2a	-0.076678	-0.0116408	-0.076678	-0.0116408
r2a	0.000287834	0.000287834	1.12794e-07	3.24112e-06



P6-26

Mole Balances : $\frac{dC_A}{dt} = r_A$ $\frac{dC_B}{dt} = r_B$ $\frac{dC_C}{dt} = r_C$

$\frac{dC_E}{dt} = r_E$ $\frac{dC_F}{dt} = r_F$

Rate Laws : $r_A = -r_1 - r_2 - r_4$ $r_B = -r_1$ $r_C = r_1 - r_2 - r_3$

$r_E = r_3 - r_4$ $r_F = r_2 + r_4$

$r_1 = \frac{wk_1 C_A C_B}{1 + K_A C_A}$ $r_2 = \frac{wk_2 C_A C_C}{1 + K_A C_A}$

$r_3 = wk_3 C_C$ $r_4 = \frac{wk_4 C_A C_E}{1 + K_A C_A}$

Stoichiometry : $C_{B0} = 0.54 \text{ kmol/dm}^3 = 540 \text{ mol/dm}^3$

from Henry's Law :

$C_{A0} = 5.9 \text{ MPa} (0.058 \text{ kmol/m}^3 \cdot \text{MPa}) = 0.3422 \text{ mol/dm}^3$

Use these equations in the following POLYMATH program to generate graphs of C_A , C_B , C_C , and C_F as a function of time.

Equations:

Initial value

$d(ca)/d(t) = ra$

0.3422

$d(cb)/d(t) = rb$

540

$d(cc)/d(t) = rc$

0

$d(ce)/d(t) = re$

0

$d(cf)/d(t) = rf$

0

$w = 10$

$k1 = 0.000468$

$Ka = 22.76$

$k2 = 0.000227$

$k4 = 0.00147$

$k3 = 0.00282$

$r3 = w * k3 * cc$

$r1 = w * k1 * ca * cb / (1 + Ka * ca)$

$r2 = w * k2 * ca * cc / (1 + Ka * ca)$

$r4 = w * k4 * ca * ce / (1 + Ka * ca)$

$rb = -r1$

$re = r3 - r4$

$rf = r2 + r4$

$ra = -r1 - r2 - r4$

$rc = r1 - r2 - r3$

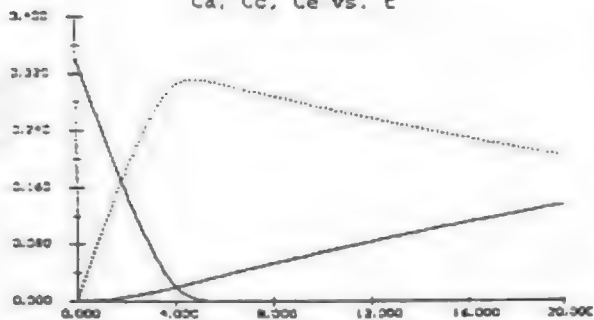
$t_0 = 0, \quad t_f = 20$

6-53

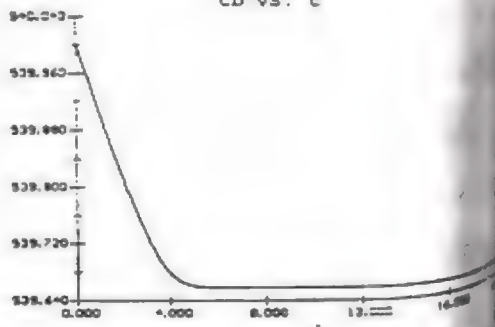
P6-26 cont'd

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	20	0	20
ca	0.3422	0.3422	9.18517e-20	9.18517e-20
cb	540	540	539.658	539.658
cc	0	0.311641	0	0.205675
ce	0	0.136398	0	0.136398
cf	0	6.37928e-05	0	6.37928e-05
w	10	10	10	10
k1	0.000468	0.000468	0.000468	0.000468
ka	22.76	22.76	22.76	22.76
k2	0.000227	0.000227	0.000227	0.000227
k4	0.00147	0.00147	0.00147	0.00147
k3	0.00282	0.00282	0.00282	0.00282
r3	0	0.00878827	0	0.00580002
r1	0.0984025	0.0984025	2.31981e-19	2.31981e-19
r2	0	1.621e-05	0	4.28838e-23
r4	0	4.96363e-06	0	1.84167e-22
rb	-0.0984025	-2.31981e-19	-0.0984025	-2.31981e-19
re	0	0.00878695	0	0.00580002
rf	0	2.07778e-05	0	2.27051e-22
ra	-0.0984025	-2.32208e-19	-0.0984025	-2.32208e-19
rc	0.0984025	0.0984025	-0.00834598	-0.00580002

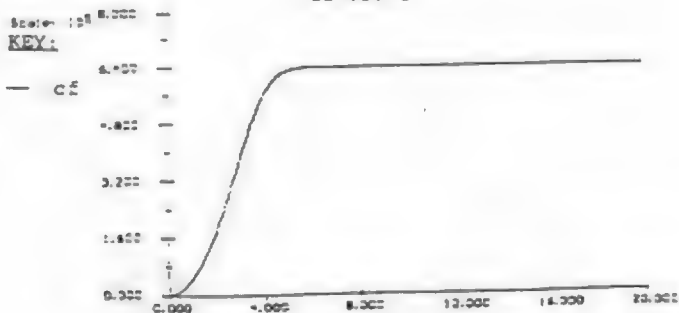
Ca, Cc, Ce vs. t



Cb vs. t

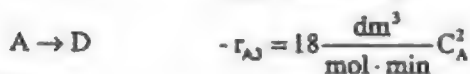


Cf vs. t



CDP6-A

Given: The following system of gas phase reactions:



Finding selectivity:

$$S_{CB} = \frac{6 \cdot C_A}{2} \quad S_{CD} = \frac{6}{18 \cdot C_A}$$

To minimize B, make C_A as high as possible. Therefore use a plug flow reactor. To minimize D, make C_A as low as possible. Therefore use a CSTR. The above two statements contradict each other. Therefore look at the numerical values.

$$C_{A0} = \frac{P_0}{RT} = \frac{405.3 \text{ kPa}}{8.314 \cdot 500 \text{ K}} = .097 \frac{\text{dm}^3}{\text{mol}}$$

and since $\delta = \delta_B + \delta_C + \delta_D = 0$,

$$C_{AF} = C_{A0}(1 - X_F) = 0.1 C_{A0}$$

Examining the ratios at final and initial conditions:

$$S_{CB0} = \frac{6 \cdot .097}{2} = 0.291$$

$$S_{CBF} = \frac{6 \cdot .1 \cdot .097}{2} = .0291$$

$$S_{CD0} = \frac{6}{18 \cdot .097} = 3.4$$

$$S_{CDF} = \frac{6}{18 \cdot .097 \cdot 0.1} = 34.4$$

r_B seems to be the undesirable dominant reaction the whole time so keeping C_A low will maximize C the best so use a CSTR. If we tried to change reactors, we would want $S_{CB} = S_{CD}$, but the only time that happens is when C_A equals $1/3$ and it never can.

$$V = \frac{F_{A0} X}{-r_A} = \frac{1 \cdot .9}{2 + 6 \cdot .097 \cdot .1 + 18 \cdot (.097)^2 \cdot .1^2} = .35 \text{ dm}^3$$

CDP6-B

a)

$$v_0 C_{A0} - v_0 C_A + r_A W = 0$$

$$-v_0 C_B + r_B W = 0$$

$$-v_0 C_C + r_C W = 0$$

$$-v_0 C_D + r_D W = 0$$

$$r_A = -k_1 C_A^2 - k_3 C_A$$

$$r_B = k_1 C_A - k_2 C_B$$

$$r_C = k_2 C_B$$

$$r_D = k_3 C_A$$

The equations:

$$f(cb) = -cb + (k1 \cdot ca + ca - k2 \cdot cb) = w/vg$$

$$f(cc) = -cc + k2 \cdot cb + w/vg$$

$$f(cd) = -cd + k3 \cdot ca + w/vg$$

$$f(ca) = ca - ca - (k1 \cdot ca + ca + k3 \cdot ca) = w/vg$$

$$k1 = .2$$

$$k2 = .8884$$

$$k3 = .8886$$

$$ca_0 = .81$$

$$vg = 2.5$$

$$w = 5888$$

$$\text{Initial values: } cb_g = 8.188 \times 10^{-2}, cc_g = 8.188 \times 10^{-2}$$

$$cd_g = 8.288 \times 10^{-3}, ca_g = 8.188 \times 10^{-2}$$

Solution

Variable	Value
cb	8.194×10^{-2}
cc	8.155×10^{-2}
cd	8.355×10^{-2}
ca	8.296×10^{-2}
k1	8.2888
k2	8.488×10^{-3}
k3	8.688×10^{-3}
ca0	8.8188
vg	2.5888
w	5888.8

c)

$$\frac{dC_A}{dW} = (r_{A1} + r_{A3}) / v_0$$

$$\frac{dC_B}{dW} = (-r_{A1} + r_{B2}) / v_0$$

$$\frac{dC_C}{dW} = -r_{B2} / v_0$$

$$\frac{dC_D}{dW} = r_{A3} / v_0$$

$$r_{A1} = -k_1 C_A$$

$$r_{B2} = -k_2 C_B$$

$$r_{A3} = -k_3 C_A$$

The equations:

$$d(ca)/d(w) = (ra1 + ra3) / vg$$

$$d(cb)/d(w) = (-ra1 + rb2) / vg$$

$$d(cc)/d(w) = -rb2 / vg$$

$$d(cd)/d(w) = -ra3 / vg$$

$$k1 = .2$$

$$ra1 = -k1 \cdot ca = ca$$

$$k2 = .8884$$

$$rb2 = -k2 \cdot cb$$

$$k3 = .8886$$

$$ra3 = -k3 \cdot ca$$

$$vg = 2.5$$

$$\text{Initial values: } w_g = 8.8, ca_g = 8.8188, cb_g = 8.8, cc_g = 8.8$$

$$cd_g = 8.8$$

$$\text{Final value: } w_f = 18888$$

$$k_1 = 0.0014 \text{ m}^3/\text{kg cat} \cdot \text{s}$$

$$k_2 = 0.00146$$

$$k_3 = 0.0000765$$

$$v_0 = 2.5$$

$$CA_0 = 0.01$$

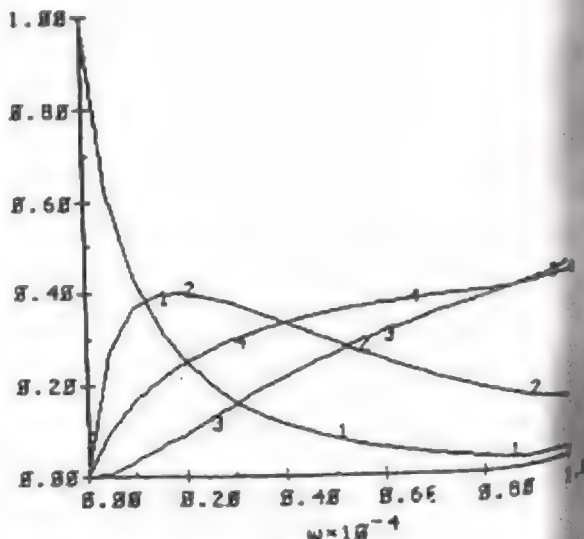
KEY:

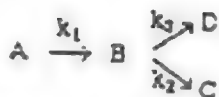
1 - ca

2 - cb

3 - cc

4 - cd

 $\times 10^2$ 



Batch reactor: $y_{A0} = 1$

(a) $k_1 = 0.01 \text{ sec}^{-1}$, $t = 1.5 \text{ min} = 90 \text{ s}$



$$N_{A0} \frac{dX}{dt} = -r_A V$$

$$C_{A0} \frac{dX}{dt} = k_1 C_A = k_1 C_{A0} (1-X)$$

$$\int_0^X \frac{dX}{1-X} = \int_0^t k_1 dt$$

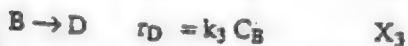
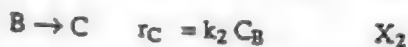
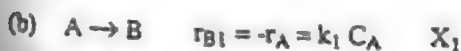
$$\ln\left(\frac{1}{1-X_1}\right) = k_1 t$$

$$\frac{1}{1-X_1} = e^{k_1 t}$$

$$X_1 = 1 - e^{-k_1 t}$$

$$C_A = C_{A0} (1-X_1) = C_{A0} e^{-k_1 t}$$

$$\frac{C_A}{C_{A0}} = e^{-k_1 t} = e^{-(0.01)(90)} = 0.41$$



$$-r_B = -r_{B1} + r_C + r_D = -k_1 C_A + k_2 C_B + k_3 C_B$$

$$\frac{dC_B}{dt} = -k_1 C_{A0} e^{-k_1 t} + (k_2 + k_3) C_B$$

$$\frac{dC_B}{dt} = -(0.01)(0.2) e^{-0.01t} + (0.003 + 0.002) C_B$$

$$\frac{dC_B}{dt} = -0.002 [1 - e^{-0.01t}] + 0.005 C_B$$

Using a Runge-Kutta Gill numerical solution, we find that, for $t = 2 \text{ min} = 120 \text{ s}$, $C_B = 0.136 \text{ gmol/dm}^3$.

$$(c) \quad \frac{dC_C}{dt} = r_C = k_2 C_B \quad ; \quad \frac{dC_C}{dt} = k_2 C_B \quad ; \quad C_C = k_2 \int_0^t C_B dt$$

From the solution in part (b), we have values of C_B at intervals as small as 5 sec, so we can use Simpson's rule to obtain C_C :

$$t = 1 \text{ min} = 60 \text{ sec.}$$

$$C_C = 0.003 \left(\frac{15}{3} \right) [0 + 4(0.0449) + 2(0.0782) + 4(0.102) + 0.1183]$$

$$C_C = 0.0129 \text{ gmol/dm}^3$$

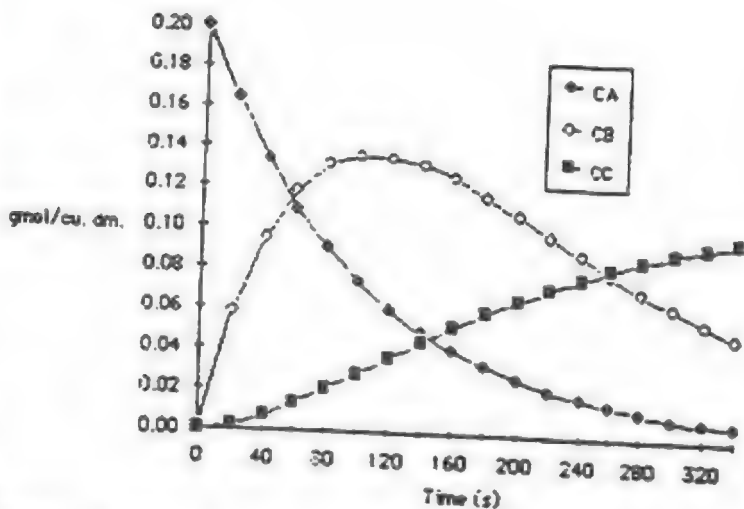
$$t = 2 \text{ min} = 120 \text{ sec}$$

$$C_C = 0.003 \left(\frac{30}{3} \right) [0 + 4(0.0782) + 2(0.1183) + 4(0.134) + 0.1355]$$

$$C_C = 0.0366 \text{ gmol/dm}^3$$

(d)

T	C_A	C_B	C_C	C_D
0	0.2	0	0	0
20	0.164	0.0572	0.0018	0.0012
40	0.134	0.0950	0.0065	0.0043
60	0.108	0.118	0.0129	0.0086
80	0.0899	0.131	0.0205	0.0136
100	0.0736	0.136	0.0285	0.0190
120	0.0602	0.135	0.0366	0.0244
140	0.0493	0.131	0.0447	0.0298
160	0.0404	0.125	0.0523	0.0349
180	0.0331	0.116	0.0595	0.0392
200	0.0271	0.107	0.0662	0.0442
220	0.0222	0.0982	0.0724	0.0482
240	0.0181	0.0890	0.0779	0.0520
260	0.0149	0.0801	0.0829	0.0553
280	0.0122	0.0717	0.0874	0.0583
300	0.00996	0.0638	0.0914	0.0609
320	0.0082	0.0566	0.0949	0.0632
340	0.0067	0.0499	0.0979	0.0635



The concentration of B is highest at $t = 110$ sec, where its value is 0.1363 gmol/dm^3 .

(e)

Balance on A:

$$F_{A0} - F_A + r_A V = 0$$

$$v C_{A0} - v C_A - k_1 C_A V = 0$$

$$C_{A0} - C_A - k_1 C_A \tau = 0$$

$$C_{A0} - C_A (1 + k_1 \tau) = 0$$

$$\frac{C_A}{C_{A0}} = \frac{1}{(1 + k_1 \tau)}$$

Balance on B:

$$F_{B0} - F_B + r_B V = 0$$

$$-v C_B + (k_1 C_A - k_2 C_B - k_3 C_B) V = 0$$

$$-C_B + k_1 C_A \tau - k_2 C_B \tau - k_3 C_B \tau = 0$$

$$C_B (1 + k_2 \tau + k_3 \tau) = k_1 \tau C_A$$

$$C_A = \frac{C_B (1 + k_2 \tau + k_3 \tau)}{k_1 \tau}$$

$$\frac{C_A}{C_{A0}} = \frac{1}{1 + k_1 \tau} = \frac{C_B (1 + k_2 \tau + k_3 \tau)}{C_{A0} k_1 \tau}$$

$$\frac{C_B}{C_{A0}} = \frac{k_1 \tau}{(1 + k_1 \tau) (1 + k_2 \tau + k_3 \tau)}$$

$\tau(s)$	10	50	100	150	200	300	500
C_B/C_{A0}	0.08	0.26	0.33	0.34	0.33	0.3	0.23

$C_{B,max}$ occurs at $\tau = 150 \Delta$

$$\therefore F_B = v C_B = \left(20 \frac{\text{dm}^3}{\text{min}}\right) (150 \Delta) \left(\frac{\text{min}}{60 \text{ sec}}\right) = 50 \text{ dm}^3/\text{min}$$

CDP6-D

First, find the values for k.

$$k_1 = 2989e^{(-10.87/(.001987 \cdot 700))} = 1.2$$

$$k_2 = 9466e^{(-15.11/(.001987 \cdot 700))} = .18$$

$$k_3 = 11127e^{(-15.06/(.001987 \cdot 700))} = .22$$

In this problem

Isobutylene = I

Methacrolein = M

CO₂ = D

CO = C

Oxygen = O

The mole balances for these species are as follows:

$$F_{I0} - F_I = (-r_{I1} - r_{I2} - r_{I3})V$$

$$F_M = r_{IM}V$$

$$F_D = r_{2D}V$$

$$F_C = r_{3D}V$$

Oxygen is in excess so we will assume that $F_O = F_{O0}$.

The rate laws for these reactions are as follows:

$$-r_{I1} = -r_{I0} = r_{IM} = k_1 C_I C_{O0}$$

$$-r_{I2} = \frac{-4r_{2D}}{25} = \frac{1}{4} r_{2D} = k_2 C_I C_{O0}$$

$$-r_{I3} = \frac{4r_{3D}}{-17} = \frac{1}{4} r_{3D} = k_3 C_I C_{O0}$$

Combine all of these and come up with the following:

$$C_{I0} - C_I = (k_1 C_I C_{O0} + k_2 C_I C_{O0} + k_3 C_I C_{O0})\tau$$

$$C_{O0} - C_O = (k_1 C_I C_{O0} + \frac{25}{4} k_2 C_I C_{O0} + \frac{17}{4} k_3 C_I C_{O0})\tau$$

$$C_M = k_1 C_I C_{O0} \tau$$

$$C_D = 4 * k_2 C_I C_{O0} \tau$$

$$C_C = 4 * k_3 C_I C_{O0} \tau$$

Before plugging into POLYMATH, evaluate the parameters and derive equations for conversion.

$$C_T = \frac{p}{RT} = \frac{2}{.082 \cdot 700} = 0.034$$

$$C_{I0} = y_{A0} C_T = .1 * .034 = 0.0034$$

$$C_{O0} = 0.031$$

$$X_I = \frac{C_{I0} - C_I}{C_{I0}}$$

$$X_{I1} = \frac{C_M}{C_{I0}}$$

$$X_{I2} = \frac{C_D}{4C_{I0}}$$

$$X_{I3} = X_I - X_{I1} - X_{I2}$$

6-60

Then plug into POLYMATH to get the following:

Equations:Initial value

$f(ci) = ci - cio + (k1 \cdot ci \cdot coo + k2 \cdot ci \cdot coo + k3 \cdot ci \cdot coo) \cdot \tau$ 0.001
 $f(cm) = k1 \cdot ci \cdot coo \cdot \tau - cm$ 0.001
 $f(cd) = 4 \cdot k2 \cdot ci \cdot coo \cdot \tau - cd$ 0.004
 $f(cc) = 4 \cdot ci \cdot coo \cdot \tau - cc$ 0.004
 $f(co) = co - coo + (k1 \cdot ci \cdot coo + 25/4 \cdot k2 \cdot ci \cdot coo + 17/2 \cdot k3 \cdot ci \cdot coo) \cdot \tau$ 0.01
 $cio = .0034$
 $k1 = 1.2$
 $coo = .031$
 $k2 = .18$
 $k3 = .22$
 $\tau = 10$
 $x1 = cm/cio$
 $x2 = .25 \cdot cd/cio$
 $x = (cio - ci)/ci$
 $x3 = x - x1 - x2$

Variable	Solution	
	Value	f()
ci	0.00227273	-1.775e-12
cm	0.000845455	1.011e-12
cd	0.000507273	-1.381e-12
cc	0.00281818	3.835e-13
cio	0.0034	
k1	1.2	
coo	0.031	
k2	0.18	
k3	0.22	
tau	10	
x1	0.248663	
x2	0.0372995	
x	0.496	
x3	0.210037	

$$X_I = 0.496 \quad X_{II} = 0.25 \quad X_{III} = 0.037 \quad X_{IV} = 0.21$$

CDP6-E

$$\frac{dC_A}{dt} = r_A$$

$$\frac{dC_B}{dt} = r_B$$

$$C_C = KC_B$$

$$r_A = k_2 C_B - k_1 C_A$$

$$r_B = k_1 C_A - k_2 C_B$$

Once that is done, then it gets plugged into POLYMATH and the composition can be found.

After 6.5 h, the answer is found to be:

$$y_A = .44$$

$$y_B = .37$$

$$y_C = .19$$

Equations:

$$d(ca)/d(t) = ra$$

$$d(cb)/d(t) = rb$$

$$cc = .5 * cb$$

$$k2 = .001$$

$$k1 = .002$$

$$ra = k2 * cb - k1 * ca$$

$$rb = k1 * ca - k2 * cb$$

$$t_0 = 0, \quad t_f = 390$$

Initial value

1

0

<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
t	0	390	0	390
ca	1	1	0.540245	0.540245
cb	0	0.459755	0	0.459755
cc	0	0.229878	0	0.229878
k2	0.001	0.001	0.001	0.001
k1	0.002	0.002	0.002	0.002
ra	-0.002	-0.000620734	-0.002	-0.000620734
rb	0.002	0.002	0.000620734	0.000620734

CDP6-F

First, find τ . To do this use the original design equation for a CSTR:

$$V = \frac{F_{A0}X}{-r_A}$$

Then since $F_{A0} = C_{A0}v_0$ and $\tau = V/v_0$ then the design equation becomes:

$$\tau = \frac{C_{A0}X}{-r_A}$$

Using the rate law and stoichiometry we find:

$$-r_A = k_1 C_{A0}(1-X)$$

Combining all these and solving for τ when $X = .3$, $C_{A0} = .1$ and $k_1 = .412$

$$\tau = \frac{C_{A0}X}{k_1 C_{A0}(1-X)} = \frac{.1 * .3}{.412 * .1 * .7} = 1.04h$$

Once that has been calculated, redo all the mole balances:

$$C_{A0} - C_A = -r_A \tau$$

$$C_{B0} - C_B = -r_B \tau$$

$$C_C = r_C \tau$$

$$C_D = r_D \tau$$

$$C_E = r_E \tau$$

Then do the rate laws:

$$-r_A = k_1 C_A$$

$$-r_B = k_1 C_A + k_2 C_C$$

$$r_C = k_1 C_A - k_2 C_C$$

$$r_D = k_1 C_A + k_2 C_C$$

$$r_E = k_2 C_C$$

Combining and rearranging into a function:

$$f(C_A) = 0 = C_A - C_{A0} + k_1 C_A \tau$$

$$f(C_B) = 0 = C_B - C_{B0} + (k_1 C_A + k_2 C_C) \tau$$

$$f(C_C) = 0 = (k_1 C_A - k_2 C_C) \tau - C_C$$

$$f(C_D) = 0 = (k_1 C_A + k_2 C_C) \tau - C_D$$

$$f(C_E) = 0 = k_2 C_C \tau - C_E$$

CDP6-F cont'd

Plug those into POLYMATH:

6-F

Equations:

$$f(ca) = ca - cao + k1 \cdot ca \cdot \tau$$

$$f(cb) = cb - cbo - (k1 \cdot ca + k2 \cdot cc) \cdot \tau$$

$$f(cc) = (k1 \cdot ca - k2 \cdot cc) \cdot \tau - cc$$

$$f(cd) = (k1 \cdot ca - k2 \cdot cc) \cdot \tau - cd$$

$$f(ce) = k2 \cdot cc \cdot \tau - ce$$

$$cao = .1$$

$$k1 = .412$$

$$\tau = 1.04$$

$$cbo = .14$$

$$k2 = .055$$

Variable	Solution	
	Value	f()
ca	0.0700045	3.361e-15
cb	0.108382	4.023e-11
cc	0.0283726	9.472e-13
cd	0.0316184	-3.405e-13
ce	0.00162291	1.579e-11
cao	0.1	
k1	0.412	
tau	1.04	
cbo	0.14	
k2	0.055	

$$C_c = .028 \text{ need } F_{co} = 10$$

$$v_0 = \frac{F_c}{C_c} = \frac{10}{.028} = 357 \text{ gal/h}$$

$$V = \tau v_0 = 1.04 \cdot 357 = 371.3 \text{ gal}$$

b) No solution will be given.

CDP6-G

First, write all of the equations in terms of symbols:

$$(1) \quad 4A + 5B \Leftrightarrow 4C + 6D$$

$$(2) \quad 4A + 3B \Leftrightarrow 2E + 6D$$

$$(3) \quad 4C + B \Leftrightarrow 2F$$

$$(4) \quad 4A + 6C \Leftrightarrow 5E + 6D$$

$$(5) \quad 2C \Leftrightarrow E + B$$

$$(6) \quad E + 2B \Leftrightarrow 2F$$

Set up a coefficient matrix:

	Species					
	A	B	C	D	E	F
(1)	-4	-5	4	6	0	0
(2)	-4	-3	0	6	2	0
(3)	0	-1	-4	0	0	2
(4)	-4	0	-6	6	5	0
(5)	0	1	-2	0	1	0
(6)	0	-2	0	0	-1	2

6-64

CDP6-G (cont'd)

Now, reduce the numbers in column 1 and rows 2,3,4,5, and 6 to 0 by adding and subtracting with row 1:

$$\begin{array}{l} (1) \begin{pmatrix} -4 & -5 & 4 & 6 & 0 & 0 \end{pmatrix} \\ (2) \begin{pmatrix} 0 & 2 & -4 & 0 & 2 & 0 \end{pmatrix} \\ (3) \begin{pmatrix} 0 & -1 & -4 & 0 & 0 & 2 \end{pmatrix} \\ (4) \begin{pmatrix} 0 & 5 & -10 & 0 & 5 & 0 \end{pmatrix} \\ (5) \begin{pmatrix} 0 & 1 & -2 & 0 & 1 & 0 \end{pmatrix} \\ (6) \begin{pmatrix} 0 & -2 & 0 & 0 & -1 & 2 \end{pmatrix} \end{array}$$

Next, repeat this for column 2, rows 3, 4, 5, and 6:

$$\begin{array}{l} (1) \begin{pmatrix} -4 & -5 & 4 & 6 & 0 & 0 \end{pmatrix} \\ (2) \begin{pmatrix} 0 & 2 & -4 & 0 & 2 & 0 \end{pmatrix} \\ (3) \begin{pmatrix} 0 & 0 & -12 & 0 & 2 & 4 \end{pmatrix} \\ (4) \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \\ (5) \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \\ (6) \begin{pmatrix} 0 & 0 & -4 & 0 & 1 & 2 \end{pmatrix} \end{array}$$

Finally, repeat for column 3, rows 4,5, and 6:

$$\begin{array}{l} (1) \begin{pmatrix} -4 & -5 & 4 & 6 & 0 & 0 \end{pmatrix} \\ (2) \begin{pmatrix} 0 & 2 & -4 & 0 & 2 & 0 \end{pmatrix} \\ (3) \begin{pmatrix} 0 & 0 & -12 & 0 & 2 & 2 \end{pmatrix} \\ (4) \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \\ (5) \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \\ (6) \begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 2 \end{pmatrix} \end{array}$$

From this final matrix it is apparent that there are four independent reactions.

We then use reactions 1, 2, 3, and 6 to define our X values:

$$\begin{aligned} X_1 &= \frac{\Delta F_{A1}}{-F_{A0}} = \frac{\Delta F_{B1}}{-1.25F_{A0}} = \frac{\Delta F_{C1}}{F_{A0}} = \frac{\Delta F_{D1}}{1.5F_{A0}} \\ X_2 &= \frac{\Delta F_{A2}}{-F_{A0}} = \frac{\Delta F_{B2}}{-0.75F_{A0}} = \frac{\Delta F_{E2}}{0.5F_{A0}} = \frac{\Delta F_{D2}}{1.5F_{A0}} \\ X_3 &= \frac{\Delta F_{C3}}{-\Theta_B F_{A0}} = \frac{\Delta F_{B3}}{-\Theta_B F_{A0}} = \frac{\Delta F_{F3}}{2\Theta_B F_{A0}} \\ X_6 &= \frac{\Delta F_{E6}}{-0.5\Theta_B F_{A0}} = \frac{\Delta F_{B6}}{-\Theta_B F_{A0}} = \frac{\Delta F_{F6}}{\Theta_B F_{A0}} \end{aligned}$$

From here we generate a Stoichiometric Table:

Species	Initial	Change	Final
A	F_{A0}	$-F_{A0}(1-X_1+X_2)$	$F_{A0}(1-X_1+X_2)$
B	$\Theta_B F_{A0}$	$-F_{A0}(1.25X_1+0.75X_2+\Theta_B X_3+\Theta_B X_6)$	$F_{A0}(\Theta_B-1.25X_1+0.75X_2+\Theta_B X_3+\Theta_B X_6)$
C	0	$F_{A0}(X_1-4\Theta_B X_3)$	$F_{A0}(X_1-4\Theta_B X_3)$
D	0	$F_{A0}(1.5X_1+1.5X_2)$	$F_{A0}(1.5X_1+1.5X_2)$
E	0	$F_{A0}(0.5X_2-0.5X_6)$	$F_{A0}(0.5X_2-0.5X_6)$
F	0	$F_{A0}(2\Theta_B X_3+\Theta_B X_6)$	$F_{A0}(2\Theta_B X_3+\Theta_B X_6)$

Balance on A:

$$\frac{dF_A}{dV} = r_A = -(-r_1 - r_2 - r_4)$$

$$F_A = F_{A0}(1 - X_1 - X_2) \Rightarrow F_{A0} \frac{dX_1}{dV} + F_{A0} \frac{dX_2}{dV} = -r_1 - r_2 - r_4$$

Balance on B:

$$-F_{A0} \left(1.25 \frac{dX_1}{dV} + 0.75 \frac{dX_2}{dV} + \Theta_B \frac{dX_3}{dV} + \Theta_B \frac{dX_6}{dV} \right) = -\frac{1}{4} r_1 - \frac{1}{4} r_2 - r_3 + \frac{1}{2} r_5 - r_6$$

Balance on C:

$$F_{A0} \left(\frac{dX_1}{dV} - 4\Theta_B \frac{dX_3}{dV} \right) = -(r_1 - 4r_3 - \frac{1}{2} r_5 - r_5)$$

Balance on F:

$$F_{A0} \Theta_B \left(2 \frac{dX_3}{dV} + \frac{dX_6}{dV} \right) = -(2r_3 + r_6)$$

Combine and simplify to get:

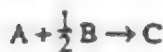
$$F_{A0} \frac{dX_1}{dV} = \frac{1}{2} r_3 + r_5 - \frac{3}{2} r_6$$

$$F_{A0} \frac{dX_2}{dV} = -r_1 - r_2 - \frac{1}{2} r_4 - r_5 - \frac{3}{2} r_6$$

$$F_{A0} \frac{dX_3}{dV} = \frac{\frac{1}{4} r_1 - r_3 - \frac{1}{2} r_5}{\Theta_B}$$

$$F_{A0} \frac{dX_6}{dV} = \frac{-\frac{1}{2} r_1 + \frac{1}{2} r_6}{\Theta_B}$$

CDP6-H



$$C_{T0} = 0.15 \text{ mol/dm}^3$$

$$k_1 C_A^0 = (0.7)(.15)^{3/2} = 0.04$$

$$k_2 C_A^0 = (0.6)(.15)^2 = 0.0135$$

$$F_{A0} = 10 \text{ mol/min}$$

$$F_{B0} = 5 \text{ mol/min}$$

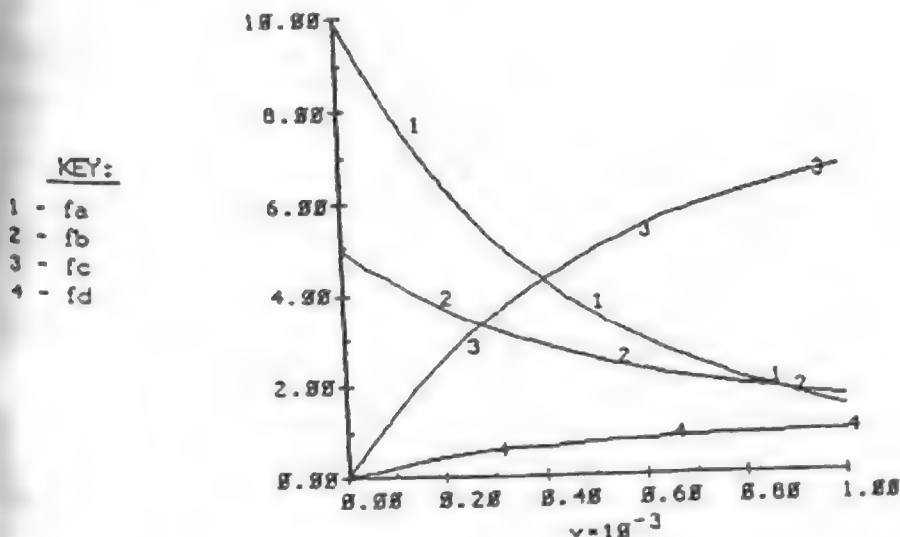
$$\frac{dF_A}{dV} = -.04 \frac{F_A}{F_T} \left(\frac{F_B}{F_T} \right)^{1/2} - .0135 \left(\frac{F_A}{F_T} \right)^2$$

$$\frac{dF_B}{dV} = -.02 \left(\frac{F_A}{F_T} \right) \left(\frac{F_B}{F_T} \right)^{1/2}$$

$$\frac{dF_C}{dV} = .04 \left(\frac{F_A}{F_T} \right) \left(\frac{F_B}{F_T} \right)^{1/2}$$

$$\frac{dF_D}{dV} = 0.00675 \left(\frac{F_A}{F_T} \right)^2$$

$$F_T = F_A + F_B + F_C + F_D + F_E$$



The equations:

$$d(fa)/d(v) = -.84 * fa * (fb/ft) = -.5/ft - .8135 * (fa/ft) = 2$$

$$d(fb)/d(v) = -.82 * fa * (fb/ft) = .5/ft$$

$$d(fc)/d(v) = .84 * fa * (fb/ft) = .5/ft$$

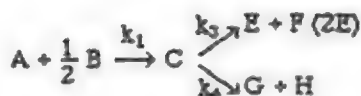
$$d(fd)/d(v) = .88675 * (fa/ft) = 2$$

$$ft = fa + fb + fc + fd$$

$$\text{Initial values: } v_g = 8.8, \quad fa_g = 18.8888, \quad fb_g = 5.88888, \quad fc_g = 8.8$$

$$fd_g = 8.8$$

$$\text{Final value: } v_f = 1888.8$$

CDP6-I

$$k_3 C_{T0} = 1.05 \times 10^{-2}$$

$$k_4 C_{T0} = 1.35 \times 10^{-2}$$

$$k_3 C_{T0} + k_4 C_{T0} = 2.4 \times 10^{-2}$$

$$\frac{dF_E}{dV} = 2.1 \times 10^{-2} \left(\frac{F_C}{F_T} \right)$$

$$\frac{dF_G}{dV} = 1.35 \times 10^{-2} \left(\frac{F_C}{F_T} \right)$$

$$\frac{dF_H}{dV} = 1.35 \times 10^{-2} \left(\frac{F_C}{F_T} \right)$$

$$\frac{dF_C}{dV} = .04 \left(\frac{F_A}{F_T} \right) \left(\frac{F_B}{F_T} \right)^{1/2} - 2.4 \times 10^{-2} \left(\frac{F_C}{F_T} \right)$$

The equations:

$$d(fa)/d(v) = -.84 * fa * (fb/ft) = -.5/ft - .8135 * (fa/ft) = 2$$

$$d(fb)/d(v) = -.82 * fa * (fb/ft) = .5/ft$$

$$d(fc)/d(v) = .84 * fa * (fb/ft) = .5/ft - .824 * (fc/ft)$$

$$d(fd)/d(v) = .88675 * (fa/ft) = 2$$

$$d(fe)/d(v) = .821 * (fc/ft)$$

$$d(fg)/d(v) = .8135 * (fc/ft)$$

$$d(fh)/d(v) = .8135 * (fc/ft)$$

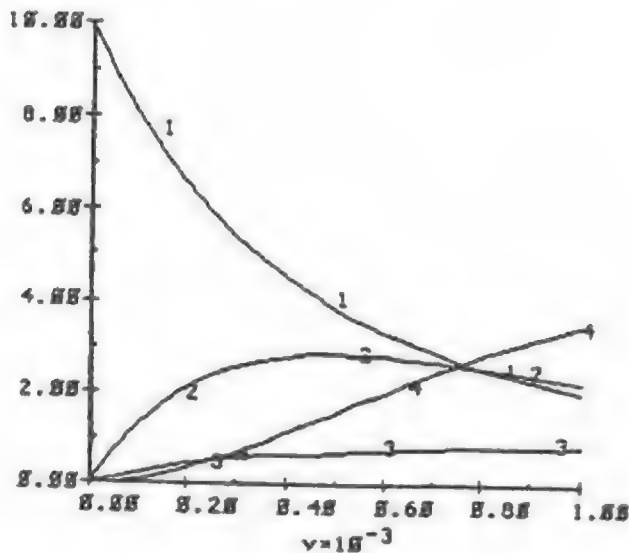
$$ft = fa + fb + fc + fd + fe + fg + fh$$

$$\text{Initial values: } v_g = 8.8, \quad fa_g = 18.8888, \quad fb_g = 5.88888, \quad fc_g = 8.8$$

$$fd_g = 8.8, \quad fe_g = 8.8, \quad fg_g = 8.8, \quad fh_g = 8.8$$

$$\text{Final value: } v_f = 1888.8$$

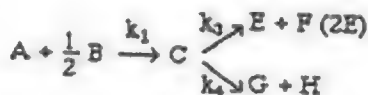
- KEY:
- 1 - fa
 - 2 - fc
 - 3 - fd
 - 4 - fe



CDP6-J

Same as 9-14, except $k_5 C_{T0} = 4.5 \times 10^{-6}$

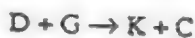
From P9-14



$$k_3 C_{T0} = 1.05 \times 10^{-2}$$

$$k_4 C_{T0} = 1.35 \times 10^{-2}$$

$$k_3 C_{T0} + k_4 C_{T0} = 2.4 \times 10^{-2}$$



$$\frac{dF_D}{dV} = .00675 \left(\frac{F_A}{F_T} \right)^2 - .45 \left(\frac{F_D}{F_T} \right) \left(\frac{F_G}{F_T} \right)$$

$$\frac{dF_K}{dV} = .45 \left(\frac{F_D}{F_T} \right) \left(\frac{F_G}{F_T} \right)$$

$$\frac{dF_C}{dV} = .04 \left(\frac{F_A}{F_T} \right) \left(\frac{F_B}{F_T} \right)^{\frac{1}{2}} + .45 \left(\frac{F_D}{F_T} \right) \left(\frac{F_G}{F_T} \right) - 2.4 \times 10^{-2} \left(\frac{F_C}{F_T} \right)$$

$$\frac{dF_G}{dV} = .0135 \left(\frac{F_C}{F_T} \right) - .45 \left(\frac{F_D}{F_T} \right) \left(\frac{F_G}{F_T} \right)$$

The equations:

$$d(fa)/d(v) = -.84 * fa * (fb/ft) ** .5/ft - .8135 * (fa/ft) ** 2$$

$$d(fb)/d(v) = -.82 * fa * (fb/ft) ** .5/ft$$

$$d(fc)/d(v) = .84 * fa * (fb/ft) ** .5/ft - .824 * (fc/ft) + p$$

$$d(fd)/d(v) = .88675 * (fa/ft) ** 2 - p$$

$$d(fe)/d(v) = .821 * (fc/ft)$$

$$d(fg)/d(v) = .8135 * (fc/ft) - p$$

$$d(fh)/d(v) = .8135 * (fc/ft)$$

$$d(fk)/d(v) = p$$

$$ft = fa + fb + fc + fd + fe + fg + fh + fk$$

$$p = .45 * (fd/ft) * (fg/ft)$$

Initial values: $v_g = 8.8$, $fa_g = 18.8888$, $fb_g = 5.88888$, $fc_g = 8.8$

$fd_g = 8.8$, $fe_g = 8.8$, $fg_g = 8.8$, $fh_g = 8.8$, $fk_g = 8.8$

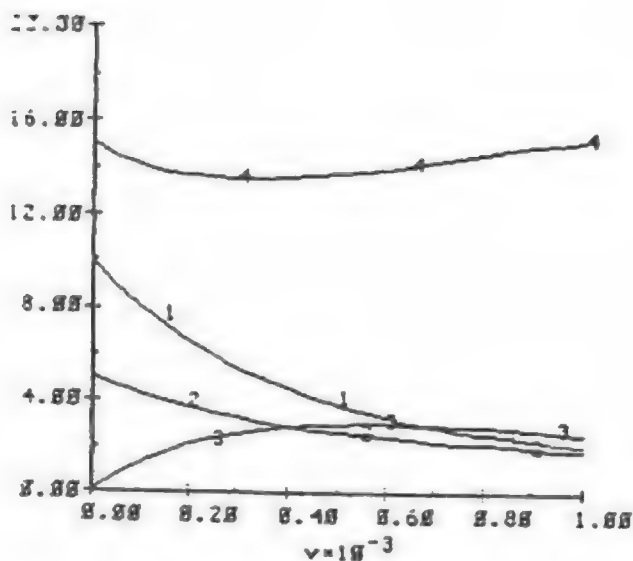
Final value: $v_f = 1288.8$

<u>v</u>	<u>fa</u>	<u>fb</u>	<u>fc</u>	<u>fd</u>
8.8	18.8888	5.88888	8.8	8.8
58.8888	8.9866	4.6328	8.7847	8.1394
188.888	8.8836	4.3888	1.2854	8.2588
158.888	7.2858	4.8828	1.7548	8.3558
288.888	6.5826	3.7368	2.1248	8.4327
258.888	5.9672	3.5883	2.4128	8.4889
388.888	5.4288	3.2985	2.6318	8.5253
358.888	4.9579	3.1846	2.7941	8.5438
488.888	4.5454	2.9396	2.9181	8.5466
458.888	4.1833	2.7931	2.9888	8.5366
588.888	3.8645	2.6626	3.8347	8.5165

<u>v</u>	<u>fa</u>	<u>fb</u>	<u>fc</u>	<u>fd</u>
588.888	3.8645	2.6626	3.8347	8.5165
558.888	3.5826	2.5461	3.8555	8.4891
688.888	3.3325	2.4416	3.8549	8.4567
658.888	3.1896	2.3478	3.8366	8.4214
788.888	2.9181	2.2638	3.8836	8.3848
758.888	2.7389	2.1863	2.9585	8.3482
888.888	2.5692	2.1166	2.9835	8.3126
858.888	2.4226	2.8538	2.8486	8.2787
988.888	2.2893	1.9947	2.7713	8.2468
958.888	2.1677	1.9413	2.6972	8.2174
1288.8	2.8563	1.8921	2.6194	8.1986

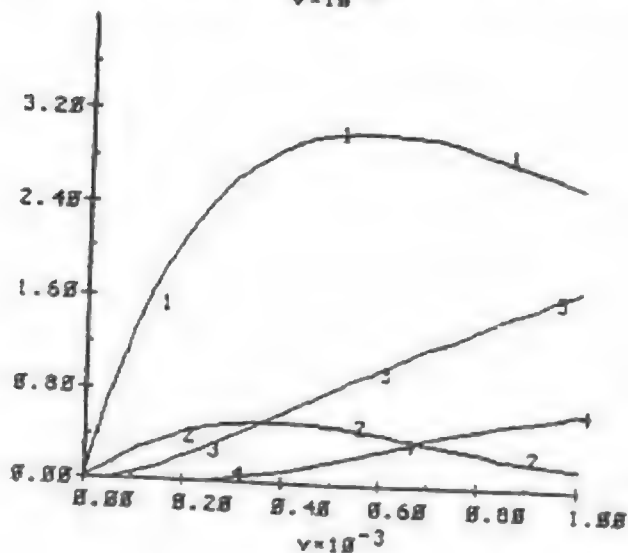
KEY:

- 1 - fa
- 2 - fb
- 3 - fc
- 4 - ft



KEY:

- 1 - fc
- 2 - fd
- 3 - fg
- 4 - fk



CDP6-K

a) Have to determine best temperature, flow rate of propylene and which reactor system. Start with both mole balances:

PBR:

$$\frac{dF_B}{dW} = r_B \quad \frac{dF_P}{dW} = r_P \quad \frac{dF_I}{dW} = r_I \quad \frac{dF_D}{dW} = r_D$$

CSTR:

$$F_{B0} - F_B = -r_B t' \quad F_{P0} - F_P = -r_P t' \quad F_I = r_I t'$$

$$F_D = r_D t'$$

Next, do the rate laws:

$$r_B = -k_1 C_B^2 C_P \quad r_P = -k_1 C_B^2 C_P - k_2 C_I C_P \quad r_I = k_1 C_B^2 C_P - k_2 C_I C_P$$

$$r_D = k_2 C_I C_P$$

Finally, the stoichiometry:

$$C_i = \frac{F_i}{v_0} \quad t' = \frac{W}{v_0}$$

To find ideal conditions, use one of the reactors to find the ideal temperature and the ideal entering flow rate of propylene. Like this example using the PBR:

6-K

Equations:

$$d(f_i)/d(\tau_{\text{aup}}) = r_i$$

$$d(f_p)/d(\tau_{\text{aup}}) = r_p$$

$$d(f_d)/d(\tau_{\text{aup}}) = r_d$$

$$d(f_b)/d(\tau_{\text{aup}}) = r_b$$

$$T=200$$

$$k_1 = 3.74e7 \cdot \exp(-7390/T)$$

$$k_2 = 3.7e7 \cdot \exp(-10000/T)$$

$$r_d = k_2 \cdot f_i^{.5} \cdot f_p^{.9}$$

$$r_b = -k_1 \cdot f_b^{.9} \cdot f_p$$

$$r_p = -k_1 \cdot f_b^{.9} \cdot f_p - k_2 \cdot f_i^{.5} \cdot f_p^{.9}$$

$$r_i = k_1 \cdot f_b^{.9} \cdot f_p - k_2 \cdot f_i^{.5} \cdot f_p^{.9}$$

$$\tau_{\text{aup}_0} = 0, \quad \tau_{\text{aup}_2} = 1e+09$$

Variable	Initial value	Maximum value	Minimum value	Final value
τ_{aup}	0	7.5e+07	0	7.5e+07
f_p	31	31	19.4466	19.4466
f_i	0	11.5534	0	11.5534
f_d	0	2.50903e-05	0	2.50903e-05
f_b	11.6	11.6	0.0466102	0.0466102
T	200	200	200	200
λ_1	3.35498e-09	3.35498e-09	3.35498e-09	3.35498e-09
k_2	7.13637e-15	7.13637e-15	7.13637e-15	7.13637e-15
r_d	0	3.50827e-13	0	3.5083e-13
r_b	-9.44201e-07	-4.13206e-09	-9.44201e-07	-4.13206e-09
r_i	9.44201e-07	9.44201e-07	4.13171e-09	4.13171e-09
r_p	-9.44201e-07	-4.13241e-09	-9.44201e-07	-4.13241e-09

CDP6-K cont'd

The best temperature is 200K and the flow rate should be 31 mol/s or 2678 kg mol/day. The τ found for the PBR is 7.5×10^7 . Using the CSTR with the same numbers it is found that the τ found is 1×10^{12} . So the PBR is better.

6-K

Equations:

$f(fb) = fb - fbo - rb \cdot \tau_{aup}$	Initial value
$f(fp) = fp - fpo - rp \cdot \tau_{aup}$	0.2
$f(fi) = ri \cdot \tau_{aup} - fi$	18
$f(fd) = rd \cdot \tau_{aup} - fd$	11
$fbo = 11.6$	0.001
$\tau_{aup} = 1e12$	
$fpo = 31$	
$T = 200$	
$k1 = 3.74e4 \cdot \exp(-7390/T)$	
$k2 = 3.7e7 \cdot \exp(-10000/T)$	
$rd = k2 \cdot fi^{.5} \cdot fp^{.9}$	
$rb = -k1 \cdot fb^{.9} \cdot fp$	
$rp = -k1 \cdot fb^{.9} \cdot fp - k2 \cdot fi^{.5} \cdot fp$	
$ri = k1 \cdot fb^{.9} \cdot fp - k2 \cdot fi^{.5} \cdot fp^{.9}$	

Variable	Value	f()
fb	0.147654	$2.29e-15$
fp	19.0934	$2.787e-15$
fi	11.1141	$1.01e-15$
fd	0.338228	$3.347e-17$
fbo	11.6	
τ_{aup}	$1e+12$	
fpo	31	
T	200	
k1	$3.35498e-12$	
k2	$7.13637e-15$	
rb	$-1.14523e-11$	
rd	$3.38228e-13$	
rp	$-1.19066e-11$	
ri	$1.11141e-11$	

CDP6-M

$$S_{DU} = \frac{206000 \exp\left(-\frac{7610}{T}\right) P_p P_c}{11.7 \exp\left(-\frac{1920}{T}\right) P_p P_c}$$

$$= 17606 \exp\left(-\frac{5690}{T}\right)$$

Notice the selectivity is completely independent of the pressures of the two reactants, therefore, the reactor could be either a PFR or CSTR without changing the selectivity.

At $T = 450^\circ\text{C}$ $S_{DU} = 6.76$

At $T = 350^\circ\text{C}$ $S_{DU} = 1.9$

So, the temperature should be at 450°C in order to maximize the selectivity.

CDP6-N

- a) To determine which reactions are necessary, make a matrix out of the reactions:

$$\begin{bmatrix} -1 & -1 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 1 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & -1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & -1 & 1 \end{bmatrix}$$

Reducing it gets this matrix:

$$\begin{bmatrix} -1 & -1 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & 0 & 1 \\ 0 & 0 & 0 & 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Therefore reaction 6 can be ignored.

- b) 1) In a packed-bed reactor, these are the mole balances:

$$\frac{dF_T}{dW} = r_T$$

$$\frac{dF_M}{dW} = r_M$$

$$\frac{dF_{PX}}{dW} = r_{PX}$$

$$\frac{dF_{MX}}{dW} = r_{MX}$$

$$\frac{dF_{OX}}{dW} = r_{OX}$$

$$\frac{dF_{TMB}}{dW} = r_{TMB}$$

CDP6-N cont'd

These are the rate laws needed.

$$r_T = \frac{-k_1 P_T P_M}{Z^2}$$

$$r_M = \frac{-k_1 P_T P_M - k_4 P_M P_{PX} - k_5 P_M P_{MX}}{Z^2}$$

$$r_{PX} = \frac{k_1 P_T P_M - k_2 P_{PX} - k_4 P_M P_{PX}}{Z^2}$$

$$r_{MX} = \frac{k_2 P_{PX} - k_3 P_{MX} - k_5 P_M P_{MX}}{Z^2}$$

$$r_{OX} = \frac{k_3 P_{MX}}{Z^2}$$

$$r_{TMB} = \frac{k_4 P_M P_{PX} + k_5 P_M P_{MX}}{Z^2}$$

Stoichiometry:

$$C_j = \frac{P_j}{RT}$$

$$C_j = C_{T0} \frac{F_j}{F_{T0}}$$

$$P_j = \frac{C_{T0} R T F_j}{F_{T0}} = \frac{P_{T0} F_j}{F_{T0}} = A F_j$$

$$A = \frac{10}{600} = .0167$$

Combining:

$$\frac{dF_T}{dW} = \frac{-k_1 A^2 F_T F_M}{Z^2}$$

$$\frac{dF_M}{dW} = \frac{-k_1 A^2 F_T F_M - k_4 A^2 F_M F_{PX} - k_5 A^2 F_M F_{MX}}{Z^2}$$

$$\frac{dF_{PX}}{dW} = \frac{k_1 A^2 F_T F_M - k_2 A F_{PX} - k_4 A^2 F_M F_{PX}}{Z^2}$$

$$\frac{dF_{MX}}{dW} = \frac{k_2 A F_{PX} - k_3 A F_{MX} - k_5 A^2 F_M F_{MX}}{Z^2}$$

$$\frac{dF_{OX}}{dW} = \frac{k_3 A F_{MX}}{Z^2}$$

$$\frac{dF_{TMB}}{dW} = \frac{k_4 A^2 F_M F_{PX} + k_5 A^2 F_M F_{MX}}{Z^2}$$

Plugging into POLYMATH gets the following graphs:

CDP6-N cont'd

6-N

Equations:

Initial value

$d(ft)/d(w)=rt$

300

$d(fm)/d(w)=rm$

300

$d(fpx)/d(w)=rpx$

0

$d(fmx)/d(w)=rmx$

0

$d(fox)/d(w)=rox$

0

$d(ftmb)/d(w)=rtmb$

0

$k1=3.9$

$z=1+3.3*.0167*fpx+13.6*.0167*fmx+33.3*.0167*fox+215*.0167*ft$

mb

$k2=.9$

$k4=1.2$

$k3=2.3$

$k5=14.5$

$rt=-k1*.0167*ft*.0167*fm/z^2$

$rox=k3*.0167*fmx/z^2$

$rtmb=(k4*.0167*fm*.0167*fpx+k5*.0167*fm*.0167*fmx)/z^2$

$rm=(-k1*.0167*ft*.0167*fm-k4*.0167*fm*.0167*fpx-k5*.0167*fm*.0167*fmx)/z^2$

$rpx=(k1*.0167*ft*.0167*fm-k2*.0167*fpx-k4*.0167*fm*.0167*fpx)/z^2$

$rmx=(k2*.0167*fpx-k3*.0167*fmx-k5*.0167*fm*.0167*fmx)/z^2$

$spx=if(rox>0)then(rpx/rox)else(0)$

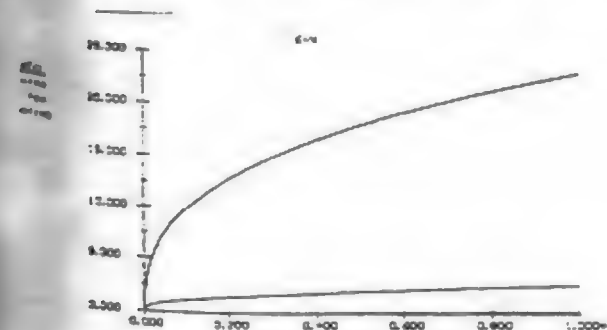
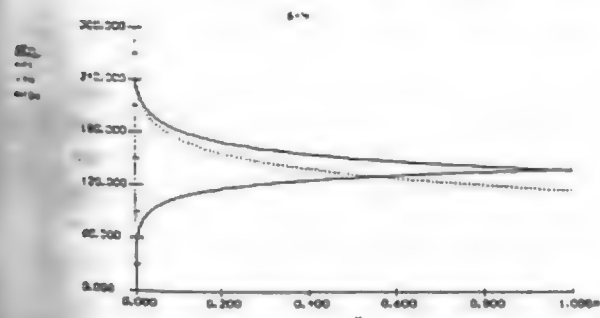
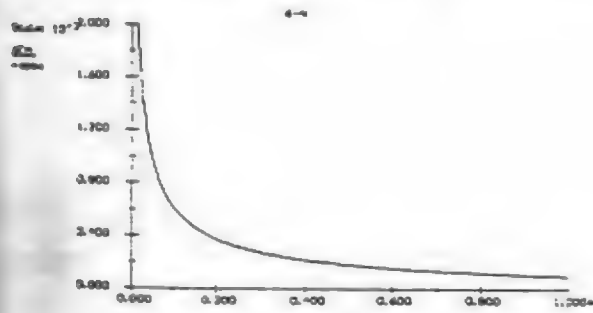
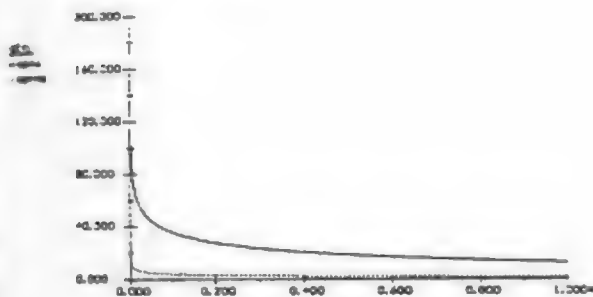
$sptmb=if(rtmb>0)then(rpx/rtmb)else(0)$

$spm=if(rmx>0)then(rpx/rmx)else(0)$

$w_0 = 0, \quad w_f = 10000$

6-N

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	10000	0	10000
ft	300	300	136.713	136.713
fm	300	300	113.87	113.87
fpx	0	137.673	0	137.673
fmx	0	1.59862	0	1.59862
fox	0	0.1722	0	0.1722
ftmb	0	22.8432	0	22.8432
k1	3.9	3.9	1.9	3.9
z	1	91.2917	1	91.2917
k2	0.9	0.9	0.9	0.9
k4	1.2	1.2	1.2	1.2
k3	2.3	2.3	2.3	2.3
k5	14.5	14.5	14.5	14.5
rt	-97.8904	-0.00203168	-97.8904	-3.30203168
rox	0	0.000143874	0	1.19763e-05
rtmb	0	0.323931	0	3.908771097
rm	-97.8904	-0.00280478	-97.8904	-3.00280478
rpx	97.8904	97.8904	0.00115388	0.00115388
rmx	0	0.046838	0	9.27257e-05
spx	0	6.55687e-08	0	95.1469
sptmb	0	4332.1	0	1.49254
spm	0	28964.4	0	12.344



CDP6-N

2)

cont'd

In a CSTR, these are the mole balances:

$$F_{T0} - F_T = -r_T W$$

$$F_{M0} - F_M = -r_M W$$

$$F_{PX} = r_{PX} W$$

$$F_{MX} = r_{MX} W$$

$$F_{OX} = r_{OX} W$$

$$F_{TMB} = r_{TMB} W$$

The rate laws are the same as the packed-bed and so is the stoichiometry, combine all of those:

$$F_{T0} - F_T = \frac{k_1 A^2 F_T F_M}{Z^2} W$$

$$F_{M0} - F_M = \frac{k_1 A^2 F_T F_M - k_4 A^2 F_M F_{PX} - k_5 A^2 F_M F_{MX}}{Z^2} W$$

$$F_{PX} = \frac{k_1 A^2 F_T F_M - k_2 A F_{PX} - k_4 A^2 F_M F_{PX}}{Z^2} W$$

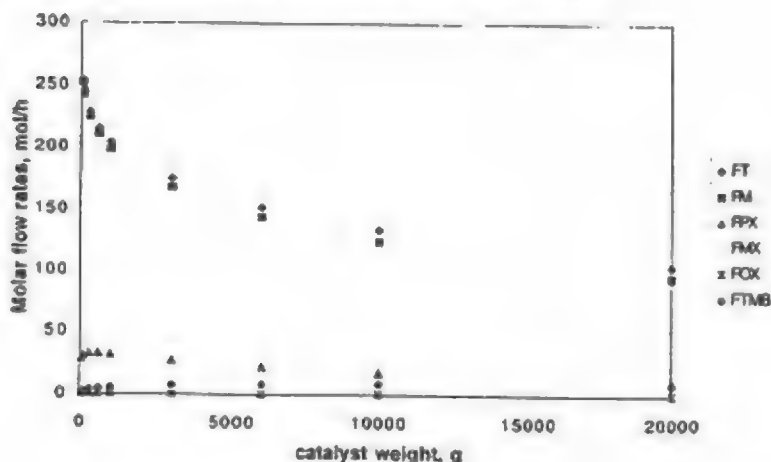
$$F_{MX} = \frac{k_2 A F_{PX} - k_3 A F_{MX} - k_5 A^2 F_M F_{MX}}{Z^2} W$$

$$F_{OX} = \frac{k_3 A F_{MX}}{Z^2} W$$

$$F_{TMB} = \frac{k_4 A^2 F_M F_{PX} + k_5 A^2 F_M F_{MX}}{Z^2} W$$

Plugging into POLYMATH gets the following graphs.

Molar flow rates vs catalyst weight



6-nb2

Equations:

$$f(ft) = ft - fto - rt \cdot w$$

$$f(fm) = fm - fmo - rm \cdot w$$

$$f(fpx) = rpx \cdot w - fpx$$

$$f(fox) = rox \cdot w - fox$$

$$f(fmx) = rmx \cdot w - fmx$$

$$f(ftmb) = rtmb \cdot w - ftmb$$

$$fto = 300$$

$$w = 20000$$

$$fmo = 300$$

$$k1 = 3.9$$

$$z = 1 + 3.3 \cdot .0167 \cdot fpx + 13.6 \cdot .0167 \cdot fmx + 33.3 \cdot .0167 \cdot fox + 215 \cdot .0167 \cdot ft$$

mb

$$k2 = .9$$

$$k4 = 1.2$$

$$k3 = 2.3$$

$$k5 = 14.45$$

$$zt = -k1 \cdot .0167 \cdot ft \cdot .0167 \cdot fm / z^2$$

$$rox = k3 \cdot .0167 \cdot fmx / z^2$$

$$rtmb = (k4 \cdot .0167^2 \cdot fm \cdot fpx + k5 \cdot .0167^2 \cdot fm \cdot fmx) / z^2$$

$$rm = (-k1 \cdot .0167 \cdot fm \cdot .0167 \cdot ft - k4 \cdot .0167 \cdot fm \cdot .0167 \cdot fpx - k5 \cdot .0167^2 \cdot fm \cdot fmx) / z^2$$

$$rpx = (k1 \cdot .0167 \cdot ft \cdot .0167 \cdot fm - k2 \cdot fpx - k4 \cdot .0167^2 \cdot fm \cdot fpx) / z^2$$

$$rmx = (k2 \cdot .0167 \cdot fpx - k3 \cdot .0167 \cdot fmx - k5 \cdot .0167^2 \cdot fm \cdot fmx) / z^2$$

$$spox = rpx / rox$$

$$sptmb = rpx / rtmb$$

$$spmx = rpx / rmx$$

Initial value

150

150

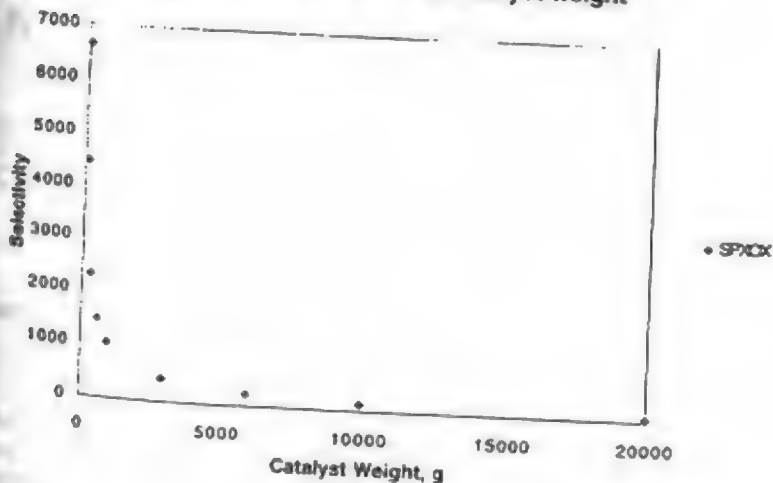
100

50

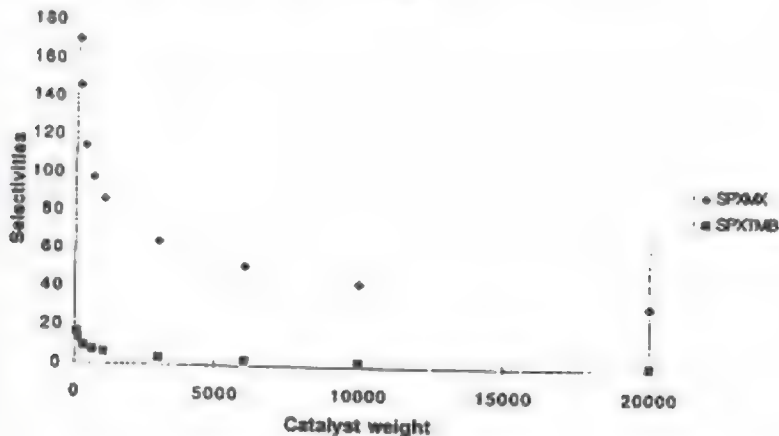
50

50

Selectivity of Px to OX vs catalyst weight



Selectivities of PX and MX and TMB vs Catalyst weight



c) Changing the ratio of Toluene to methanol finds the maximum of PX occurs at a ratio of 1.5 to 1. Changing the Concentration of the entering (changing A) stream finds that the concentration of PX increases as the total concentration increases.

Finding the maximum of MX works the same way and the ratio is 1.61 to 1 and again higher concentration yields more desired product.

ratio	P_{PX}
1	139.7
1.048896552	141.6
1.14245714	142.3
1.222222222	144.7
1.30769231	145.73
1.4	148.4
1.5	148.76
1.60889565	148.86
A	
0.0167	148.76
0.033	151.6
0.05	153.3
0.067	154.4
0.083	155
0.1	155.4
0.117	155.7
0.133	155.9
0.15	156
0.167	156.2
0.183	156.3
0.2	156.9

ratio	P_{MX}
1	11.8
0.93344387	6.25
1.048896552	17.4
1.14245714	25
1.222222222	30.2
1.30769231	33.4
1.4	35.6
1.5	38.7
1.60889565	37.1
1.72727273	37
A	
0.0167	37.1
0.033	38.4
0.05	40.1
0.067	40.3
0.083	40.7
0.1	40.8
0.117	40.9
0.133	41
0.15	41

d) Increasing the temperature shows that the ratio to maximize PX gets smaller and is now about 1.14 to 1 at 675°C. Increasing the temperature does the same thing it just makes even more of the product.

T=675	
Ratio	F _{px}
1	205.1
1.4	203.8
0.71428571	179.2
1.04896552	207.8
1.14285714	208
1.22222222	208.6

Ratio	F _{px}
1	21.3
1.04896552	29.8
1.14285714	34.1
1.22222222	35.8
1.30769231	38
1.4	39.7

A	
Ratio	F _{px}
0.0187	208
0.033	210.8
0.05	215.3
0.067	217.7
0.082	219.2
0.1	220.6
0.117	221.3
0.133	222.2
0.15	223.8
0.167	224.4
0.183	225.8
0.2	226.5
0.217	227.5
0.233	228.5
0.25	229.1
0.267	229.3
0.3	229.6
0.333	229.8
0.367	229.9
0.4	229.9
0.433	229.7
0.467	229.8
0.5	229.7
0.58	227.3
0.6	227.4
0.7	227.7
0.8	227.88
0.9	228.1
1	228.3

Similarly, maximizing MX at the new temperature gets a ratio of 1.31 to 1 and again the concentration increases.

e) No solution will be given.

CDP6-O

Mole Balances:

$$F_P = F_{P0} + r_P W \Rightarrow f(C_P) = C_P - C_{P0} - r_P \tau'$$

$$F_O = r_O W \Rightarrow f(C_O) = C_O - r_O \tau'$$

$$F_A = r_A W \Rightarrow f(C_A) = C_A - r_A \tau'$$

$$F_B = r_B W \Rightarrow f(C_B) = C_B - r_B \tau'$$

$$F_C = r_C W \Rightarrow f(C_C) = C_C - r_C \tau'$$

Rate Laws:

$$r_A = \frac{k_1 C_P C_O^{1/2}}{k_2 C_O^{1/2} + (k_1 + \frac{2}{3} k_2 + \frac{1}{3} k_3) C_P}$$

$$k_1 = 688e^{-77,500/RT} \quad k_2 = 3.5 \times 10^{-4} e^{-1312/RT} \quad k_3 = 32.8e^{-72,600/RT} \quad k_4 = 4 \times 10^4 e^{-88,000/RT}$$

Stoichiometry:

$$r_A = r_{A1} \quad r_B = \frac{1}{3} r_{A2} \quad r_C = \frac{2}{3} r_{A3} \quad r_P = -r_{A1} - r_{A2} - r_{A3} \quad r_O = -r_{A1} - \frac{2}{3} r_{A2} - \frac{1}{3} r_{A3}$$

Use these equations in the following POLYMATH program. Vary T and plot the generated values to make the desired graph. Varying the initial concentrations of P and O reveals that the selectivity of acrolein is independent of the feed composition.

CDP6-Q (cont'd)

Equations:

f(cp)=cp-cpo-rp*tau
f(co)=co-coo-ro*tau
f(ca)=ca-ra*tau
f(cb)=cb-rb*tau
f(cc)=cc-rc*tau

cpo=0.9

tau=1

coo=0.1

R=8.3144

T=900

S=ca/(cb+cc+1e-10)

k1=688*exp(-77500/R/T)

k2=3.5e-4*exp(-1312/R/T)

k3=32.8*exp(-72630/R/T)

ka=4e4*exp(-88000/R/T)

ra1=k1*cp*co**(1/2)/(ka*co**(1/2)+(k1+(9/2)*k2+(3/2)*k3)*cp)

ra2=k2*cp*co**(1/2)/(ka*co**(1/2)+(k1+(9/2)*k2+(3/2)*k3)*cp)

ra3=k3*cp*co**(1/2)/(ka*co**(1/2)+(k1+(9/2)*k2+(3/2)*k3)*cp)

ra=ra1

rb=ra2/3

rc=2/3*ra3

rp=-ra1-ra2-ra3

ro=-ra1-2/9*ra2-4/3*ra3

Initial value

0.9

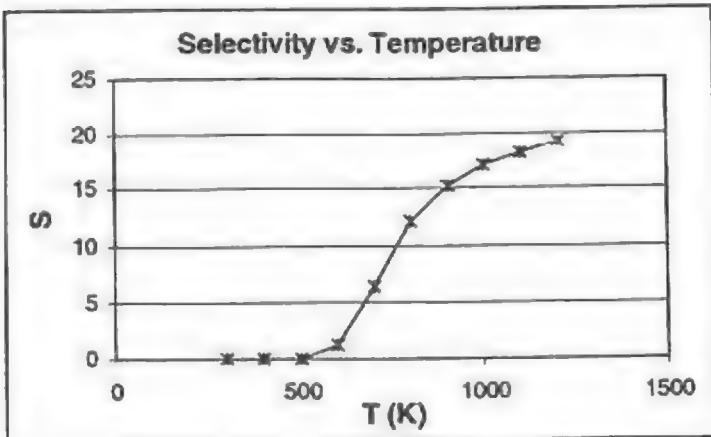
0.1

0

0

0

Variable	Value	Unit	Variable	Value	Unit
ca	0.095033		rb	0.00070173	
cb	3.019532		rc	0.00199757	
cc	3.019504		rp	-0.049766	
co	0.00070173		ro	-0.0306676	
cp	0.00070173				
cpo	0.9				
tau	1				
coo	0.1				
R	8.3144				
T	900				
S	15.2863				
k1	0.0218605				
k2	0.000793713				
k3	0.00199757				
ka	0.012117				
ra1	0.019044				
ra2	0.000603201				
ra3	0.00111884				
rp	0.049766				



Chapter 7

- P7-1.** An open-ended problem that requires students to create and original problem and solution.
- P7-2.** "What if. . ." problem. Part (a) is usually assigned because the student can load the living examples E7-2 directly on to the computer and determine when the PSSH FAILS. Also ask the students to plot the concentration of all intermediates a function of time.

Problems P7-3, P7-4, P7-5, P7-6, P7-7, and P7-8. all involve the PSSH.

- P7-3.** Is usually assigned in the graduate course.
- P7-4.** Is the easiest of the PSSH problems. Good reinforcement of PSSH principles.
- P7-5.** Requires some imagination to realize there is an intermediate NO_3 that is formed.
- P7-6.** Fairly difficult problem.
- P7-7.** True problem concerning motor oil degradation. At the undergraduate level only parts (a), (b), and (c) are assigned.
- P7-8.** Just for fun.

Problems P7-9, P7-10, P7-11, P7-12, P7-13, and P7-14. are problems concerning enzymatic reactions.

- P7-9.** Real data supplied by General Mills. Somewhat open-ended.
- P7-10.** Good graduate level problem on enzymatic reactions. There is an inconsistency in the journal article.
- P7-11.** Straight forward problem to calculate V_{max} and K_m .
- P7-12.** Involves enzyme inhibition. This problem is actually solved on the CD-ROM Professional Book Shelf material.
- P7-13.** This problem on enzyme substrate inhibition is often assigned because the CSTR has multiple steady states.
- P7-14.** Fairly straight forward problem to calculate V_{max} and determine which type of enzyme inhibition is occurring.

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Problems P7-15 through P7-23. involve polymerization and are currently only assigned at the graduate level. At the undergraduate senior level, one might assign P7-17 and/or P7-20. Most problems are quite long.

P7-24. Straight forward reinforcement of Monod kinetics in a batch reactor. Fairly short problem using POLYMATH.

P7-25. A fairly straight forward, but time consuming, problem to plot the data.

P7-26. Straight forward problem using POLYMATH.

P7-27. Very short (Ca. 10 min.) problem.

P7-28. This problem shows an important application of biomass in the petroleum industry. That of bacteria profile modification (BPM). Fairly time consuming yet realistic to plot and analyze all the data.

P7-29. Very short problem to reinforce the principles of Monod kinetics.

P7-30. Fairly straight forward new (1997) problem using POLYMATH. The student should be asked to go beyond what is asked in the problem statement by carrying out a parameter variation and sensitivity analysis.

P7-31. Shows the application of bacteria growth to degrade toxic chemicals. The problem is somewhat open-ended.

P7-32. Straight forward problem using POLYMATH. Could also ask the student to do a sensitivity analysis.

CDP7-A Alternative to P7-5 and P7-6.

CDP7-B Alternative to P7-6.

CDP7-C Alternative to P7-13.

CDP7-D Fairly straight forward.

CDP7-E Assigned at the graduate level.

CDP7-F Seldom assigned.

CDP7-G Advanced problem on bacterial growth.

CDP7-H Not assigned at undergraduate level.

CDP7-I Assigned every so often.

CDP7-J Fairly straight forward.

Summary

	<u>Assigned</u>	<u>Alternates</u>	<u>Difficulty</u>	<u>Time</u>	<u>Solution Given</u>
P7-1					No
● P7-2			SF	70	Partial(a)
● P7-3	AA	4,5,6	FSF	50	Yes
P7-4	AA	3,5	SF	40	Yes
● P7-5	AA	6,7,8,A,B	SF	30	Yes
P7-6	AA	5,7,8,A,B	FSF	35	Yes
P7-7	AA	5,6,8,A,B	FSF	70	Yes
P7-8	AA	5,6,7,A,B	SF	20	Yes
P7-9	G		MD	60	Yes
P7-10	G		MD	45	Yes
● P7-11	AA	14	SF	30	Yes
P7-12	AA	13,14,C,D	SF	50	Yes
P7-13	O	12,14,C,D	FSF	45	Yes
P7-14	O	12,13,C,D	FSF	50	Yes
P7-15	G	21	SF	45	Yes
P7-16	G		FSF	75	Yes
P7-17	G	23,E	MD	90	Yes
P7-18	G	19,22	MD	90	Yes
P7-19	G	18,22	MD	60	Yes
P7-20	G		FSF	60	Yes
P7-21	G	15	FSF	75	Yes
P7-22	G	19	MD	90	Yes
P7-23	G	17	MD	90	Yes
● P7-24	AA	26,30,32,J	SF	40	Yes
P7-25	O	28	FSF	60	Yes
P7-26	AA	24,30,32,J	SF	40	Yes
P7-27	O	29	SF	40	Yes
P7-28	I	25	FSF	60	Yes
P7-29	O	27	SF	40	Yes
P7-30	AA	24,26,37,J	SF	30	Yes
P7-31	G		MD	50	Yes
P7-32	AA	24,26,30,J	FSF	60	Yes
CDP7-A	AA	5,6,7,8,B	SF	40	Yes
CDP7-B	AA	5,6,7,8,A	SF	40	Yes
CDP7-C	AA	12,13,14,D	SF	50	Yes
CDP7-D	AA	12,13,14,C	FSF	50	Yes
CDP7-E	G	17,23	MD	60	Yes
CDP7-F	G		MD	75	Yes
CDP7-G	O		MD	60	Yes
CDP7-H	I		MD	70	Yes
CDP7-I	O		MD	60	Yes
CDP7-J	AA	24,26,30,32	FSF	45	Yes

Assigned

● = Always assigned, AA = Always assign one from the group of alternates,
O = Often, I = Infrequently, S = Seldom, G = Graduate level

Alternates

In problems that have a dot in conjunction with AA means that one of the problems, either the problem with a dot or any one of the alternates are always assigned.

Time

Approximate time in minutes it would take a B/B* student to solve the problem.

Difficulty

SF = Straight forward reinforcement of principles (plug and chug)

FSF = Fairly straight forward (requires some manipulation of equations or an intermediate calculation).

IC = Intermediate calculation required

M = More difficult

OE = Some parts open-ended.

Note the letter problems are found on the CD-ROM. For example A = CDP1-A.

Summary Table Ch-7

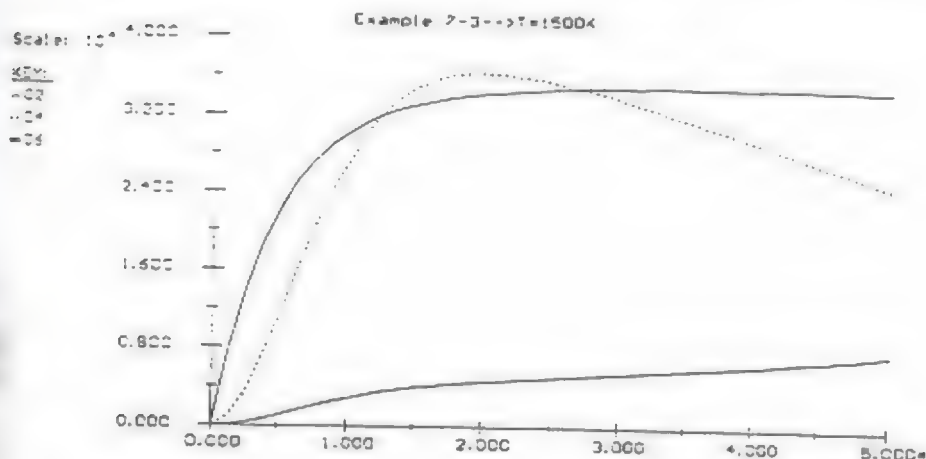
	PSSH	Enzymes	Polymerization	Cell Growth
	2(a),3,4,5,6,7,8	9,10,11,12,13,14	16,17,18,19,20, 21,22,23	24,25,26,27,28
Open-ended	2(a)	10		31
Straight forward	4,7(a),(b),(c)	11		24,29,30
Fairly Straight Forward				
More Difficult				
Parameter Variation				

Chapter 7

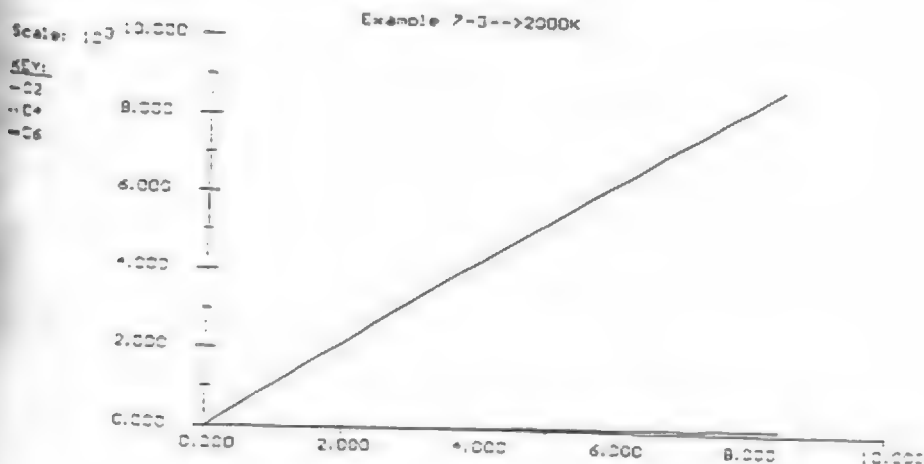
P7-1 No solution will be given.

P7-2

- (a) Use the same POLYMATH program as Example 7-2 with the appropriate temperatures. Generate the following graphs:

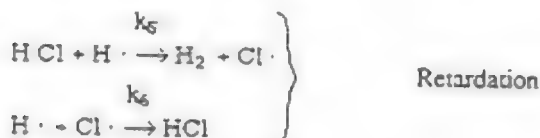
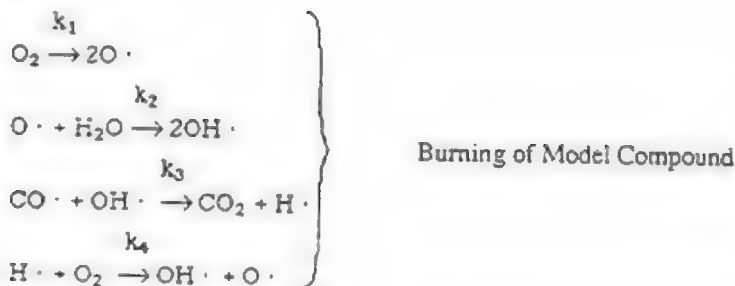


For $T = 1500$ K, steady-state is not reached, so PSSH is not valid.



For $T = 2000$ K, steady-state is not reached, so PSSH is not valid.

P7-3: Burning



$$\boxed{-r_{\text{CO}} = r_{\text{CO}_2} = k_3 (\text{CO})(\text{OH}\cdot)}$$

$$r_{\text{O}\cdot} = 0 = 2k_1 (\text{O}_2) - k_2 (\text{O}\cdot)(\text{H}_2\text{O}) + k_4 (\text{H}\cdot)(\text{O}_2)$$

then

$$(\text{O}\cdot) = \frac{2k_1 (\text{O}_2) + k_4 (\text{H}\cdot)(\text{O}_2)}{k_2 (\text{H}_2\text{O})}$$

$$r_{\text{OH}\cdot} = 0 = 2k_2 (\text{O}\cdot)(\text{H}_2\text{O}) - k_3 (\text{CO})(\text{OH}\cdot) + k_4 (\text{H}\cdot)(\text{O}_2)$$

then

$$(\text{OH}\cdot) = \frac{2k_2 (\text{O}\cdot)(\text{H}_2\text{O}) + k_4 (\text{H}\cdot)(\text{O}_2)}{k_3 (\text{CO})}$$

substituting for $(\text{O}\cdot)$

$$(\text{OH}\cdot) = \frac{2k_2 (\text{H}_2\text{O}) \frac{2k_1 (\text{O}_2) + k_4 (\text{H}\cdot)(\text{O}_2)}{k_2 (\text{H}_2\text{O})} + k_4 (\text{H}\cdot)(\text{O}_2)}{k_3 (\text{CO})}$$

$$(\text{OH}\cdot) = \frac{4k_1 (\text{O}_2) + 3k_4 (\text{H}\cdot)(\text{O}_2)}{k_3 (\text{CO})}$$

$$-r_{\text{CO}} = r_{\text{CO}_2} = k_3 (\text{CO})(\text{OH}\cdot)$$

$$\boxed{-r_{\text{CO}} = 4k_1 (\text{O}_2) + 3k_4 (\text{H}\cdot)(\text{O}_2)}$$

$$r_{\text{H}\cdot} = \overbrace{k_3 (\text{CO})(\text{OH}\cdot)}^{r_{\text{CO}_2}} - k_4 (\text{H}\cdot)(\text{O}_2) - k_5 (\text{HCl})(\text{H}\cdot) - k_6 (\text{Cl}\cdot)(\text{H}\cdot)$$

$$r_{\text{Cl}\cdot} = 0 = k_5 (\text{HCl})(\text{H}\cdot) - k_6 (\text{H}\cdot)(\text{Cl}\cdot)$$

P7-3 (cont'd)

$$Cl \cdot = \frac{k_5 (HCl)}{k_6}$$

$$r_{H\cdot} = 4k_1 (O_2) + 3k_4 (H\cdot) (O_2) - k_4 (H\cdot) (O_2) - 2k_5 (HCl) (H\cdot)$$

$$r_{H\cdot} = 4k_1 (O_2) + 2k_4 (O_2) - k_5 (HCl) (H\cdot)$$

$$r_{H\cdot} = a + b (H\cdot)$$

Constant Volume

$$e^{-bt} \frac{dC_{H\cdot}}{dt} - C_{H\cdot} \cdot b \cdot e^{-bt} = a e^{-bt}$$

$$\frac{dC_{H\cdot}}{dt} = a + b C_{H\cdot}$$

Using the integrating factor

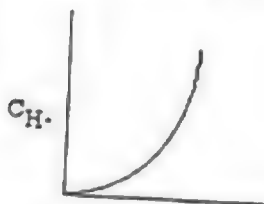
$$\frac{d(e^{-bt} C_{H\cdot})}{dt} = a e^{-bt}$$

$$C_{H\cdot} = -\frac{a}{b} + K_1 e^{bt}$$

$$t=0 \quad C_{H\cdot} = 0 \quad \text{therefore } K_1 = \frac{a}{b}$$

$$C_{H\cdot} = \frac{a}{b} [e^{bt} - 1]$$

If $k_4 (O_2) > k_5 (HCl)$, then "b" is positive



If $k_5 (HCl) > k_4 (O_2)$, then "b" is negative



P7-3 (cont'd)

$$\frac{dC_{CO}}{dt} = r_{CO} = -[4k_1(O_2) + 3k_4(H\cdot)(O_2)]$$

$$= -a - p(C_{H\cdot})$$

$$= -a - p\left[\frac{a}{b}e^{bt} - 1\right]$$

$$p(C_{H\cdot}) = 3k_4(O_2)C_{H\cdot}$$

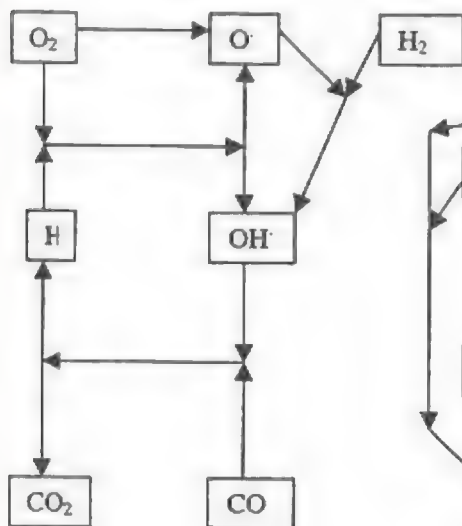
$$p = 3k_4(O_2)$$

$$a = 4k_1(O_2)$$

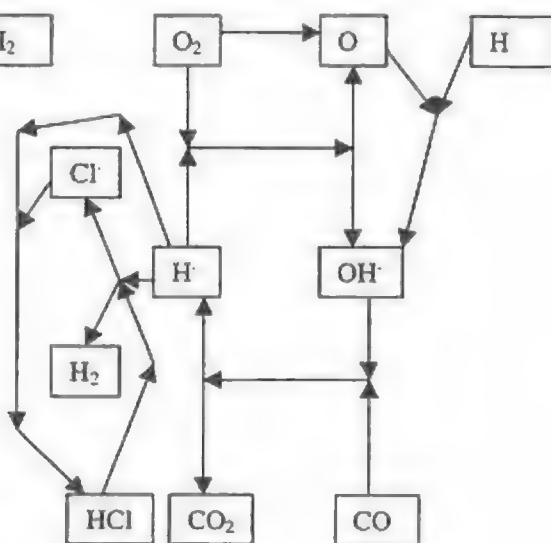
$$t=0 \quad C_{CO} = C_{CO,0}$$

$$C_{CO} = C_{CO,0} - at - p\frac{a}{b^2}e^{bt} + pt$$

Reaction Pathway w/o HCL



Reaction Pathway with HCL



P7-4

The reaction sequence is:



$$r_1 = k_1 C_{AC}$$

$$r_2 = k_2 C_{AC} C_{CH_3\cdot}$$

$$r_3 = k_3 C_{CHO\cdot} C_{AC}$$

$$r_4 = k_4 C_{CH_3\cdot}^2$$

P7-4 (cont'd)

$$-r_{AC} = r_1 + r_2 + r_3 = k_1 C_{AC} + k_2 C_{AC} C_{CH_3} + k_3 C_{AC} C_{CHO}$$

$$= C_{AC} [k_1 + k_2 C_{CH_3} + k_3 C_{CHO}]$$

(1)

Active intermediates:



$$-r_{CH_3} = -r_1 + r_2 - r_3 + \frac{1}{2} r_4 = 0$$

$$= -k_1 C_{AC} + k_2 C_{AC} C_{CH_3} - k_3 C_{CHO} C_{AC} - k_2 C_{AC} C_{CH_3} + \frac{1}{2} k_4 C_{CH_3}^2$$

$$= -k_1 C_{AC} + k_2 C_{AC} C_{CH_3} - k_3 C_{CHO} C_{AC} + \frac{1}{2} k_4 C_{CH_3}^2$$

(2)

$$-r_{CHO} = -r_1 + r_3 = -k_1 C_{AC} + k_3 C_{CHO} C_{AC} = 0$$

$$\text{or } C_{CHO} = \frac{k_1}{k_3}$$

(3)

Substituting (3) in (2) gives:

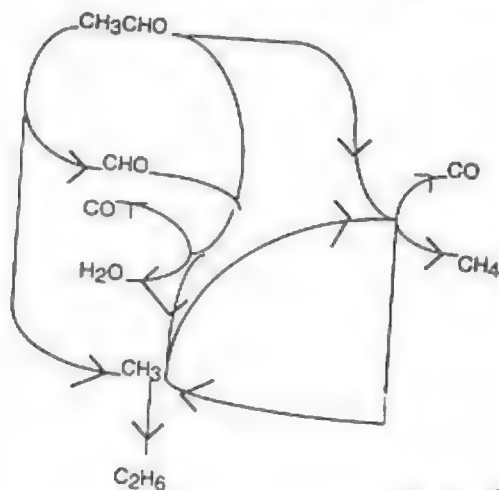
$$\frac{k_4 C_{CH_3}^2}{2} = k_1 C_{AC} + k_3 C_{CHO} C_{AC} = k_1 C_{AC} + k_1 C_{AC} = 2k_1 C_{AC}$$

$$\text{or } C_{CH_3} = 2(C_{AC})^{1/2} \left(\frac{k_1}{k_4} \right)^{1/2}$$

$$-r_{AC} = C_{AC} \left[k_1 + 2k_2 \left(\frac{k_1}{k_4} \right)^{1/2} (C_{AC})^{1/2} + \frac{k_1}{k_3} \right]$$

$$= k_1 C_{AC} \left[1 + \frac{2k_2}{\sqrt{k_1 k_4}} \sqrt{C_{AC}} + \frac{k_1}{k_3} \right]$$

With $\frac{k_2}{\sqrt{k_1 k_4}} \gg 1$ or $C_{AC} \gg 1$, $-r_{AC} \propto (C_{AC})^{3/2}$ as suggested by equation (7-2).



Gas phase reaction



with third order kinetics and an apparent negative activation energy. Consider the following mechanism, in which NO_3 is an active intermediate.



$$-r_{NO} = -r_1 - r_2$$

$$= -k_1[NO][O_2] + k_{-1}[NO_3] - k_2[NO][NO_3]$$

$$r_{NO_3} = r_1 - r_2$$

$$= k_1[NO][O_2] - k_{-1}[NO_3] - k_2[NO][NO_3]$$

$$[NO_3] = \frac{k_1[NO][O_2]}{k_{-1} + k_2[NO]}$$

$$-r_{NO} = -k_1[NO][O_2] + (k_{-1} - k_2[NO]) \frac{k_1[NO][O_2]}{k_{-1} + k_2[NO]}$$

$$= \frac{-k_1 k_2 [NO]^2 [O_2] - k_{-1} k_2 [NO]^2 [O_2]}{k_{-1} + k_2 [NO]}$$

$$= \frac{-2k_1 k_2 [NO]^2 [O_2]}{k_{-1} + k_2 [NO]}$$

$$k_{-1} \gg k_2 [NO]$$

$$-r_{NO} = -\frac{2k_1 k_2}{k_{-1}} [NO]^2 [O_2]$$

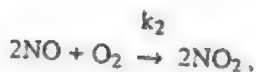
For the overall activation energy to be negative,

$$-(E_1 + E_2) + E_{-1} = E_{ov} < 0$$

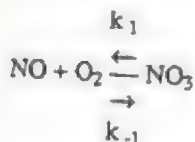
$$\Rightarrow E_{-1} < (E_1 + E_2)$$

As long as all energies are positive values.

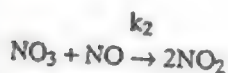
P7-5 Gas phase reaction



with third order kinetics and an apparent negative activation energy. Consider the following mechanism, in which NO_3 is an active intermediate:



$$r_1 = k_1 [\text{NO}][\text{O}_2] - k_{-1} [\text{NO}_3]$$



$$r_2 = k_2 [\text{NO}][\text{NO}_3]$$

$$r_{\text{NO}} = -r_1 - r_2 = -k_1 [\text{NO}][\text{O}_2] + k_{-1} [\text{NO}_3] - k_2 [\text{NO}][\text{NO}_3]$$

$$-r_{\text{NO}_3} \equiv 0 = r_1 - r_2 = k_1 [\text{NO}][\text{O}_2] - k_{-1} [\text{NO}_3] - k_2 [\text{NO}][\text{NO}_3]$$

$$\text{or } [\text{NO}_3] = \frac{k_1 [\text{NO}][\text{O}_2]}{k_{-1} + k_2 [\text{NO}]} ; -r_{\text{NO}} = -k_1 [\text{NO}][\text{O}_2] + (k_{-1} - k_2 [\text{NO}]) \frac{k_1 [\text{NO}][\text{O}_2]}{k_{-1} + k_2 [\text{NO}]}$$

$$r_{\text{NO}} = \frac{-k_{-1} k_1 [\text{NO}][\text{O}_2] - k_1 k_2 [\text{NO}]^2 [\text{O}_2] + k_1 k_2 [\text{NO}][\text{O}_2] - k_{-1} k_1 [\text{NO}]^2 [\text{O}_2]}{-k_1 + k_2 [\text{NO}]}$$

$$r_{\text{NO}} = \frac{-2k_1 k_2 [\text{NO}]^2 [\text{O}_2]}{k_1 + k_2 [\text{NO}]} \text{ with } k_{-1} \gg k_2 [\text{NO}], r_{\text{NO}} = \frac{-2k_1 k_2 [\text{NO}]^2 [\text{O}_2]}{k_{-1}}$$

If $k_i \propto \exp\left(\frac{-E_i}{RT}\right)$ Then for the overall activation energy to be negative,

$$\ln\left(\frac{k_1 k_2}{k_{-1}}\right) = \frac{-E_1 + E_2 - E_{-1}}{RT} = E_{\text{ov}} < 0 \text{ or } E_1 + E_2 > E_{-1}$$

P7-6 Given decomposition of O_3 in an inert gas:

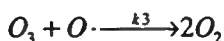
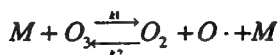
$$-r_{\text{O}_3} = \frac{k [\text{O}_3]^2 [\text{M}]}{[\text{O}_2][\text{M}] + k' [\text{O}_3]}$$

O_2 , M and O_3 appear in the denominator, active species suggested is O .
Applying rule 3 of table 7-1 to O_2 and O_3 :



P7-6 (cont'd)

O_3 and M appear in the numerator. Applying rule 1 of Table 7-1 to O_3 : $O_3 \rightarrow O_2 + O\cdot$
If the second and third equations are combined, and M is added to each side of the equation:



A mechanism is proposed which satisfies all the rules of thumb:

$$r_{O_3} = -r_1 + r_2 - r_3 = -k_1[M][O_3] + k_2[O_2][O\cdot][M] - k_3[O\cdot][O_3] = 0$$

$$r_{O_2} = r_1 - r_2 - r_3 = k_1[M][O_3] - k_2[O_2][O\cdot][M] - k_3[O\cdot][O_3] = 0$$

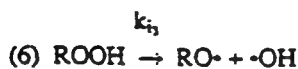
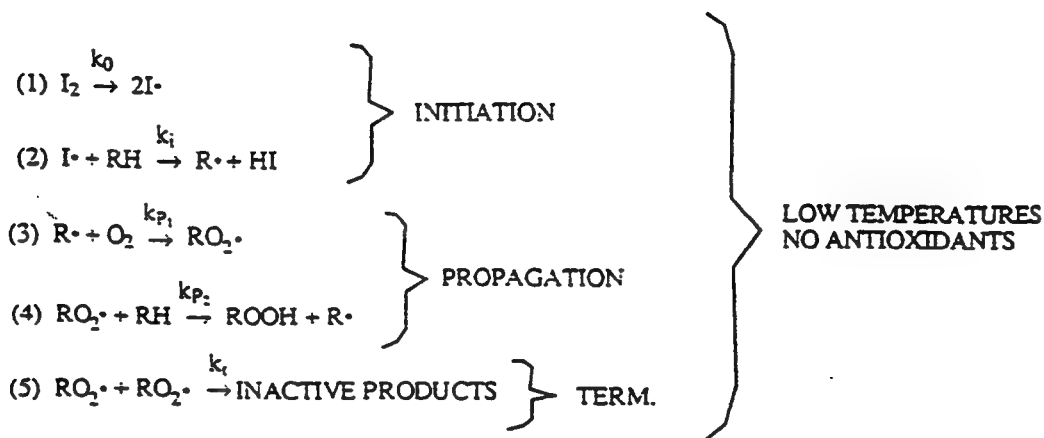
$$[O\cdot] = \frac{k_1[M][O_3]}{k_2[O_2][M] + k_3[O_3]}$$

$$\text{Then } r_{O_3} = -k_1[M][O_3] + \frac{k_1 k_2 [M]^2 [O_3][O_2] - k_1 k_3 [M][O_3]^2}{k_2 [O_2][M] + k_3 [O_3]}$$

$$r_{O_3} = \frac{-k_1 k_2 [M]^2 [O_3][O_2] + k_1 k_2 [M]^2 [O_3][O_2] - 2k_1 k_3 [M][O_3]^2}{k_2 [O_2][M] + k_3 [O_3]}$$

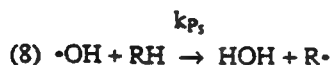
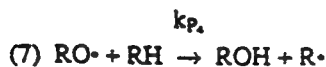
$$r_{O_3} = \frac{-2k_1 k_3 [M][O_3]^2}{k_2 [O_2][M] + \frac{k_3}{k_2} [O_3]} \quad \text{with } k = \frac{2k_1 k_3}{k_2} \text{ and } k' = \frac{k_3}{k_2}$$

P7-7



INITIATION
PROPAGATION

HIGHER TEMPERATURES
NO ANTIOXIDANTS



LOW TEMPERATURES - NO ANTIOXIDANT

$$\frac{d[I\cdot]}{dt} = r_i = 2k_0[I_2] - k_i[I\cdot][RH] \quad (A)$$

$$\frac{d[RH]}{dt} = -k_i[I\cdot][RH] - k_{p1}[RO_2\cdot][RH] \quad (B)$$

$$\frac{d[RO_2\cdot]}{dt} = k_{p1}[R\cdot][O_2] - k_{p2}[RO_2\cdot][RH] - k_t[RO_2\cdot]^2 \quad (C)$$

$$\frac{d[R\cdot]}{dt} = k_i[RH][I\cdot] - k_{p1}[R\cdot][O_2] + k_{p2}[RO_2\cdot][RH] \quad (D)$$

PSSA $\frac{d[RADICALS]}{dt} = 0$

$$(A) = 0 \quad r_i = 0 \quad [I\cdot] = \frac{2k_0[I_2]}{k_i[RH]}$$

$$\frac{d[R\cdot]}{dt} = 0 = k_i[RH][I\cdot] - k_{p1}[R\cdot][O_2] + k_{p2}[RO_2\cdot][RH]$$

↑

$$\frac{2k_0[I_2]}{k_i[RH]}$$

$$[R\cdot] = \frac{2k_0[I_2] + k_{p2}[RO_2\cdot][RH]}{k_{p1}[O_2]} \quad \text{still need to eliminate } [RO_2\cdot]$$

$$\frac{d[RO_2\cdot]}{dt} = 0 = k_{p1}[R\cdot][O_2] - k_{p2}[RO_2\cdot][RH] - k_t[RO_2\cdot]^2$$

Substitute for $[R\cdot]$:

$$2k_0[I_2] - k_t[RO_2\cdot]^2 = 0$$

$$[RO_2\cdot] = \sqrt{\frac{2k_0[I_2]}{k_t}}$$

Now substitute the expressions for the radicals into $\frac{d[RH]}{dt}$ the expression for the degradation of the oil.

$$\frac{d[RH]}{dt} = -k_i \left[\frac{2k_0[I_2]}{k_i[RH]} \right] [RH] - k_{p2} \left[\frac{2k_0[I_2]}{k_t} \right]^{1/2} [RH]$$

↓
[I·]

$$= 2k_0[I_2] - \left[\frac{2k_{p2}^2[k_0]}{k_t} \right]^{1/2} [I_2]^{1/2} [RH]$$

P7-7 (cont'd)

$$\frac{d[R\cdot]}{dt} = k_i [RH][I\cdot] - k_{p1} [R\cdot][O_2] + k_{p2} [RO_2\cdot][RH] \text{ (same)}$$

$$\frac{d[A\cdot]}{dt} = k_{A1} [AH][RO_2\cdot] - k_{A2} [A\cdot][RO_2\cdot]$$

$$\frac{d[RH]}{dt} = -k_i [I\cdot][RH] - k_{p2} [RO_2\cdot][RH]$$

Apply PSSH:

$$\frac{d[I\cdot]}{dt} = 0 \quad [I\cdot] = \frac{2k_0 [I_2]}{k_i [RH]}$$

$$\frac{d[A\cdot]}{dt} = 0 \Rightarrow [A\cdot] = \frac{k_{A1} [AH]}{k_{A2}}$$

$$\frac{d[R\cdot]}{dt} = 0 \quad [R\cdot] = \frac{2k_0 [I_2] + k_{p2} [RO_2\cdot][RH]}{k_{p1} [O_2]}$$

$$\frac{d[RO_2\cdot]}{dt} \equiv 0 \quad 2k_0 [I_2] - k_i [RO_2\cdot]^2 - 2(k_{A1} [AH][RO_2\cdot])$$

$$\therefore -k_i [RO_2\cdot]^2 - 2k_{A1} [AH][RO_2\cdot] + 2k_0 [I_2] = 0$$

$$k_i [RO_2\cdot]^2 + (2k_{A1} [AH])[RO_2\cdot] - 2k_0 [I_2] = 0 \quad \text{Quadratic in } [RO_2\cdot]$$

$$[RO_2\cdot] = \frac{-2k_{A1} [AH] \pm \sqrt{(2k_{A1} [AH])^2 + 8k_i k_0 [I_2]}}{2k_i} \quad [RO_2\cdot] \text{ MUST be positive}$$

Now (FINALLY!), let's substitute into $\frac{d[RH]}{dt}$:

$$\frac{d[RH]}{dt} = -k_i [I\cdot][RH] - k_{p2} [RO_2\cdot][RH]$$

$$\frac{d[AH]}{dt} = -k_{A1} [AH][RO_2\cdot] = -k_{A1} [AH] \frac{-2k_{A1} [AH] + \sqrt{(2k_{A1} [AH])^2 + 8k_i k_0 [I_2]}}{2k_i}$$

$$\frac{d[RH]}{dt} = -2k_0 [I_2] - k_{p2} [RH] \frac{-2k_{A1} [AH] + \sqrt{(2k_{A1} [AH])^2 + 8k_i k_0 [I_2]}}{2k_i}$$

P7-7 (cont'd)

ODE to be solved- low temperatures, no antioxidant:

$$\frac{d[RH]}{dt} = 2k_0[I_2] + \left[\frac{2k_p^2[k_0]}{k_t} \right]^{1/2} [I_2]^{1/2} [RH]$$

HIGH TEMPERATURE, NO ANTIOXIDANT

$$\frac{d[RH]}{dt} = -k_i[I\cdot] - k_{p_2}[RO_2\cdot][RH] - k_{p_1}[RO\cdot][RH] - k_{p_3}[OH\cdot][RH]$$

PSSA

$$\frac{d[I\cdot]}{dt} = 2k_0[I_2] - k_i[RH][I\cdot] = 0 \Rightarrow [I\cdot] = \frac{2k_0[I_2]}{k_i[RH]}$$

$$\frac{d[RO_2\cdot]}{dt} = k_{p_1}[O_2][R\cdot] - k_{p_2}[RO_2\cdot][RH] - k_t[RO_2\cdot]^2$$

$$\frac{d[R\cdot]}{dt} = k_i[I\cdot][RH] - k_{p_1}[R\cdot][O_2] - k_{p_2}[RO_2\cdot][RH] + k_{p_1}[RO\cdot][RH] + k_{p_3}[OH\cdot][RH]$$

$$\frac{d[RO\cdot]}{dt} = k_{i_1}[ROOH] - k_{p_4}[RO\cdot][RH]$$

$$\frac{d[OH\cdot]}{dt} = k_{i_2}[ROOH] - k_{p_5}[OH\cdot][RH]$$

USE PSSA: $\frac{d[X\cdot]}{dt} = 0$

$$\frac{d[RO\cdot]}{dt} = 0 \Rightarrow [RO\cdot] = \frac{k_{i_1}[ROOH]}{k_{p_4}[RH]}$$

$$\frac{d[R\cdot]}{dt} = 0 \Rightarrow [R\cdot] = \frac{k_i[I\cdot][RH] + k_{p_2}[RO_2\cdot][RH] + k_{p_1}[RO\cdot][RH] + k_{p_3}[OH\cdot][RH]}{k_{p_1}[O_2]}$$

$$\frac{d[OH\cdot]}{dt} = 0 \Rightarrow [OH\cdot] = \frac{k_{i_2}[ROOH]}{k_{p_5}[RH]}$$

$$\frac{d[RO_2\cdot]}{dt} = 0 = k_{p_1}[O_2][R\cdot] - k_{p_2}[RO_2\cdot][RH] - k_t[RO_2\cdot]^2$$

Substitute for $[R\cdot]$:

$$0 = 2k_0[I_2] + k_{p_3}[OH\cdot][RH] + k_{p_1}[OH\cdot][RH] - k_t[RO_2\cdot]^2$$

Now substitute for $[RO\cdot]$ and $[OH\cdot]$:

$$0 = 2k_0[I_2] + k_{i_1}[ROOH] + k_{i_2}[ROOH] - k_t[RO_2\cdot]^2$$

$$[RO_2\cdot] = \sqrt{\frac{2k_0[I_2] + 2k_{i_1}[ROOH]}{k_t}}$$

7-15

P7-7 (cont'd)

Now back to the $\frac{d[RH]}{dt}$ equation:

$$\frac{d[RH]}{dt} = -2k_0[I_2] - k_{p2}[RH] \left[\frac{2k_0[I_2] + 2k_{i1}[ROOH]}{k_t} \right]^{1/2} - k_{i1}[ROOH] - k_{i2}[ROOH]$$

or

$$\frac{d[RH]}{dt} = -2k_0[I_2] - 2k_{i1}[ROOH] - k_{p2}[RH] \left[\frac{2k_0[I_2] + 2k_{i1}[ROOH]}{k_t} \right]^{1/2}$$

Now let's look at $\frac{d[ROOH]}{dt}$

$$\frac{d[ROOH]}{dt} = k_{p1}[RO_2^{\bullet}][RH] - k_{i1}[ROOH]$$

$$\frac{d[ROOH]}{dt} = k_{p1}[RH] \left[\frac{2k_0[I_2] + 2k_{i1}[ROOH]}{k_t} \right]^{1/2} - k_{i1}[ROOH]$$

Remember, we also have:

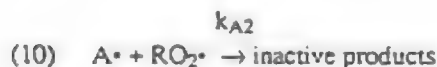
$$\frac{d[I_2]}{dt} = -k_0[I_2]$$

$$\text{or } [I_2] = [I_2]_0 e^{-k_0 t}$$

Now, let's look at the situation with anti-oxidants present:

LOW TEMPERATURES WITH ANTI-OXIDANTS

Additional reactions:



Equations:

$$\frac{d[I^{\bullet}]}{dt} = 2k_0[I_2] - k_t[I^{\bullet}][RH]$$

$$\frac{d[RO_2^{\bullet}]}{dt} = k_p[R^{\bullet}][O_2] - k_{p2}[RO_2^{\bullet}][RH] - k_{A1}[RO_2^{\bullet}][AH] - k_{A2}[A^{\bullet}][RO_2^{\bullet}]$$

P7-7 (cont'd)

HIGH TEMPERATURES WITH ANTIOXIDANTS

$$\frac{d[I\cdot]}{dt} \equiv 0 \Rightarrow [I\cdot] = \frac{2k_0[I_2]}{k_1[RH]}$$

$$\frac{d[RO\cdot]}{dt} \equiv 0 = k_{i1}[ROOH] - k_{p1}[RO\cdot][RH] \Rightarrow [RO\cdot] = \frac{k_{i1}[ROOH]}{k_{p1}[RH]}$$

$$\frac{d[OH\cdot]}{dt} \equiv 0 = k_{i1}[ROOH] - k_{p3}[RH][OH\cdot] \Rightarrow [OH\cdot] = \frac{k_{i1}[ROOH]}{k_{p3}[RH]}$$

$$\frac{d[R\cdot]}{dt} = k_1[I\cdot][RH] - k_{p1}[R\cdot][O_2] + k_{p2}[RO_2\cdot][RH] + k_{p4}[RO\cdot][RH] + k_{p5}[OH\cdot][RH]$$

$$\frac{d[RO_2\cdot]}{dt} = k_{p1}[O_2][R\cdot] - k_{p2}[RO_2\cdot][RH] - k_t[RO_2\cdot]^2 - k_{A1}[RO_2\cdot][AH] - k_{A2}[RO_2\cdot][A\cdot]$$

$$\frac{d[A\cdot]}{dt} = k_{A1}[AH][RO_2\cdot] - k_{A2}[RO_2\cdot][A\cdot]$$

Apply PSSA: $\frac{d[R\cdot]}{dt} = 0$

$$[R\cdot] = \frac{2k_0[I_2] + k_{p2}[RO_2\cdot][RH] + k_{p4}[RO\cdot][RH] + k_{p5}[OH\cdot][RH]}{k_{p1}[O_2]}$$

$$\frac{d[A\cdot]}{dt} = 0 \quad [A\cdot] = \frac{k_{A1}[AH][RO_2\cdot]}{k_{A2}[RO_2\cdot]} = \frac{k_{A1}[AH]}{k_{A2}} = [A\cdot]$$

Now substitute into $\frac{d[RO_2\cdot]}{dt}$ expression:

$$2k_0[I_2] + k_{p2}[RO_2\cdot][RH] + k_{p4}[OH\cdot][RH] - k_t[RO_2\cdot]^2 - 2(k_{A1}[RO_2\cdot][AH]) = 0$$

$$2k_0[I_2] + 2(k_{i1}[ROOH]) - k_t[RO_2\cdot]^2 + 2(k_{A1}[RO_2\cdot][AH]) = 0$$

$$k_t[RO_2\cdot]^2 + 2(k_{A1}[RO_2\cdot][AH]) - (2k_0[I_2] + k_{i1}[ROOH]) = 0$$

$$[RO_2\cdot] = \frac{-2k_{A1}[AH] \pm \sqrt{4(k_{A1}[AH])^2 + 8k_t(k_0[I_2] + k_{i1}[ROOH])}}{2k_t} = 0$$

P7-7 (cont'd)

$$\therefore [RO_2^\bullet] = \frac{-2k_{A1}[AH] + \sqrt{4(k_{A1}[AH])^2 - 8k_0 k_0[I_2] + k_{i1}[ROOH]}}{2k_t} = 0$$

Now finally,

$$\frac{d[RH]}{dt} = -k_i[I^\bullet][RH] - k_{p1}[RO_2^\bullet][RH] - k_{p2}[RO^\bullet][RH] - k_{p3}[OH^\bullet][RH]$$

$$\frac{d[RH]}{dt} = -2k_0[I_2] - 2k_{i1}[ROOH] - k_{p1}[RH] \left[\frac{-2k_{A1}[AH] + \sqrt{4(k_{A1}[AH])^2 - 8k_0 k_0[I_2] + k_{i1}[ROOH]}}{2k_t} \right]$$

$$\frac{d[AH]}{dt} = -k_{A1}[AH][RO_2^\bullet] = -k_{A1}[AH] \left[\frac{-2k_{A1}[AH] + \sqrt{4(k_{A1}[AH])^2 - 8k_0 k_0[I_2] + k_{i1}[ROOH]}}{2k_t} \right]$$

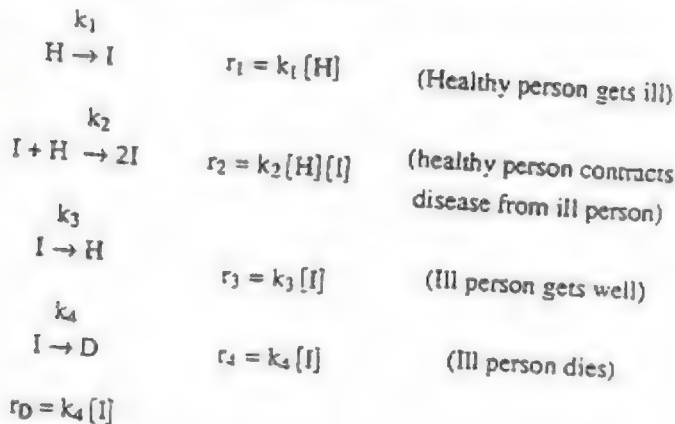
$$\frac{d[ROOH]}{dt} = k_{p1}[RO_2^\bullet][RH] - k_{i1}[ROOH] + k_{A1}[RO_2^\bullet][AH]$$

$$\frac{d[ROOH]}{dt} = -k_{i1}[ROOH] + \{k_{p1}[RH] + k_{A1}[AH]\} \left[\frac{-2k_{A1}[AH] + \sqrt{4(k_{A1}[AH])^2 - 8k_0 k_0[I_2] + k_{i1}[ROOH]}}{2k_t} \right]$$

Finally:

$$\frac{d[ROOH]}{dt} = -k_{i1}[ROOH] + \{k_{p1}[RH] + k_{A1}[AH]\} \left[\frac{-2k_{A1}[AH] + \sqrt{4(k_{A1}[AH])^2 - 8k_0 k_0[I_2] + k_{i1}[ROOH]}}{2k_t} \right]$$

P7-8 Given: Illness mechanism



Applying pseudo steady state hypothesis to I: $r_1 = r_2 - r_3 - r_4 = 0$

$$\text{or } k_1 [H] + k_2 [H][I] - k_3 [I] - k_4 [I] = 0 \quad \text{or } [I] = \frac{k_1 [H]}{(k_3 + k_4) - k_2 [H]}$$

$$\therefore r_D = \frac{k_1 k_4 [H]}{k_3 + k_4 - k_2 [H]} \quad \text{at } [H] = \frac{k_3 + k_4}{k_2} \text{ the death rate becomes infinite.}$$

It is enlightening to calculate r_H :

$$r_H = -r_1 - r_2 + r_3 = -k_1 [H] - k_2 [H][I] + k_3 [I] = -k_1 [H] - (k_2 [H] - k_3)[I]$$

$$r_H = \frac{-k_1 k_4 [H]}{(k_3 + k_4 - k_2 [H])} = -r_D < 0$$

This expression states that for every person who is ill and dies, a healthy person becomes ill. For the population as a whole, "illness is but a 'way station' on the road to 'death'." Note further that $r_H < 0$, and therefore the population will die off eventually. Initially, the death rate will be slow, until $[H] \rightarrow (k_3 + k_4) / k_2$. The model neglects the possibility of birth. In practice, it would appear to be useful in describing epidemic-like diseases, which occur over a short time so that the birth rate can be neglected.

P7-9

- a) Starting with the design equation for a batch reactor

$$\frac{dC_p}{dt} = r_p$$

$$r_p = kC$$

$$C = (C_{s0} - C_p) \left(1 - \frac{C_p}{1.4} \right)$$

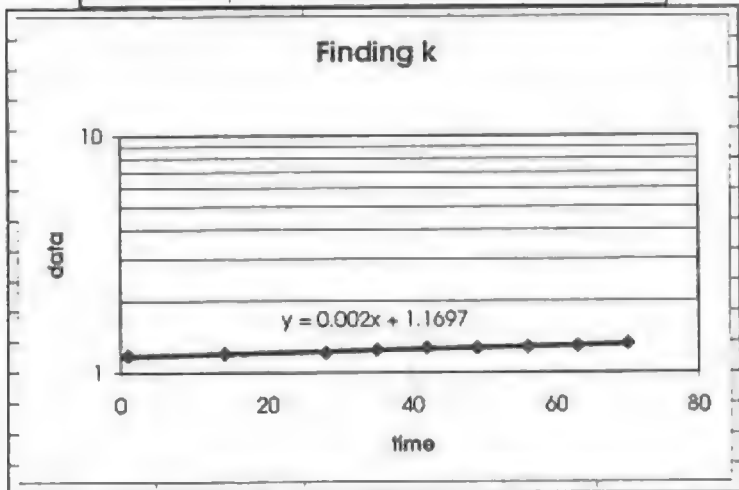
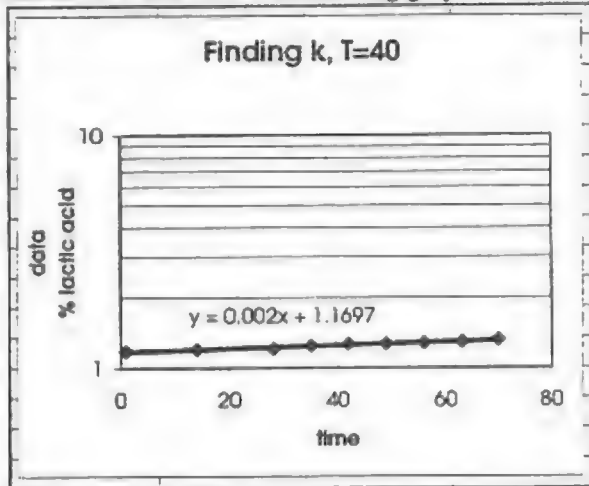
$$\frac{dC_p}{dt} = k [C_{s0} - C_p] \left[1 - \frac{C_p}{1.4} \right]$$

integrating

$$\ln \left(.933 \frac{C_p - 1.5}{C_p - 1.4} \right) = 7.14kt + C$$

P7-9 cont'd

Using the data at 40°F and 45°F the following graphs are made:



from these: $k_{40} = 2.8 \times 10^{-4}$ $C_{40} = 1.1697$

$k_{45} = 8.26 \times 10^{-4}$ $C_{45} = 1.1883$

The activation energy then is:

$$\ln \left(.933 \frac{C_p - 1.5}{C_p - 1.4} \right) = 7.14kt + C$$

$$E = - \frac{R \ln(k_2/k_1)}{1/T_2 - 1/T_1} = 108120 \frac{\text{Btu}}{\text{mol}}$$

b)

$$k_{38} = k_{45} 10^{\left(\frac{-E}{2.3R} \left(\frac{1}{497} - \frac{1}{504} \right) \right)} = 1.8 \times 10^{-4}$$

Using interpolation, $C = 1.18086$

Using the same equation used on the graphs we can solve for t when $C_p = 1.1$
 $t = 49$ days.

7-20

P7-9 cont'd

c)

$$k_{77} = k_{35} 10^{\left(\frac{-E}{2.3R} \left(\frac{1}{536} - \frac{1}{504} \right) \right)} = .0023$$

$$C = 1.211$$

$$t = 2 \text{ days}$$

d) No solution will be given.

P7-10

Michaelis-Menton Kinetics:

$$-r_1 = \frac{V_{\max} C_S}{K_m + C_S}$$

$$K_m = 6.2 \times 10^{-2} \text{ ml/ml} = 6.2\%$$

$$V_{\max} = 5.6 \frac{\mu\text{mol}}{\text{ml} \cdot \text{min}} \quad E = 40 \text{ mg}$$

Mole Balance:

$$-\frac{dC_S}{dt} = \frac{V_{\max} C_{S\%}}{K_m + C_{S\%}}$$

$$C_{S\%} = C_{S0\%}(1 - X) \Rightarrow x = \frac{1.4 - 0.2}{1.4} = 0.86$$

Where $C_{S\%}$ is the percent of fish oil.

For most oils:

$$C_T = \frac{\text{density}}{\text{MW}} = \frac{0.9}{300} = 3 \times 10^{-3} \text{ mol/ml} = 3 \times 10^3 \mu\text{mol/ml}$$

$$C_S = C_T C_{S\%}$$

$$\Rightarrow \int_{1.4}^{0.2} \frac{K_m + C_{S\%}}{C_{S\%}} dC_{S\%} = \int_0^1 \frac{V_{\max}}{C_T} dt = \int_0^1 \frac{5.6 \times 10^{-3}}{3} dt$$

$$\Rightarrow K_m \ln\left(\frac{1.4}{0.2}\right) + (1.4 - 0.2) = \frac{5.6 \times 10^{-3}}{3} t$$

$$\Rightarrow t = \frac{6.2 \ln(7) + 1.2}{5.6 \times 10^{-3}/3} \text{ min} = 7106 \text{ min} = 118.4 \text{ hrs}$$

P7-11

(a) Given: The enzyme catalyzed reaction of the decomposition of hydrogen peroxide. For a batch reactor:

$$\frac{1}{V} \frac{dN_S}{dt} = \frac{dC_S}{-dt} = r_S = \frac{-V_{\max} C_S}{K_m + C_S} \quad \text{at } t=0, C_S = C_{S0}$$

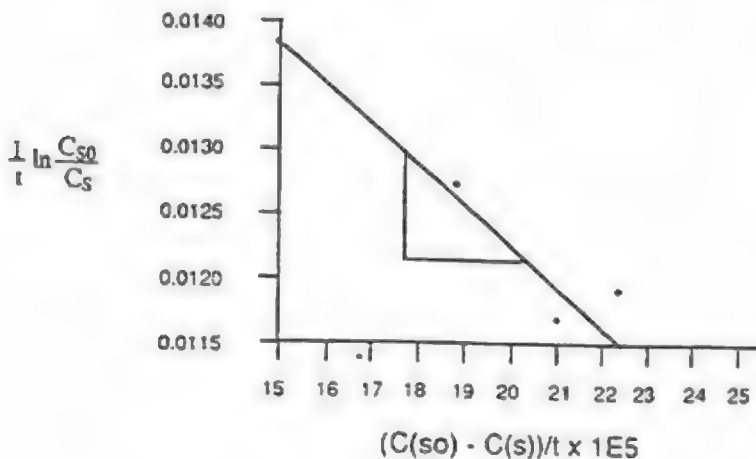
Rearranging and integrating:

$$\int_{C_{S0}}^{C_S} \left[\frac{K_m}{C_S} + 1 \right] dC_S = - \int_0^t V_{\max} dt = K_m \ln \frac{C_S}{C_{S0}} + C_S - C_{S0} = -V_{\max} t$$

$$\text{or } \frac{1}{t} \ln \frac{C_{S0}}{C_S} = - \frac{C_{S0} - C_S}{K_m t} + \frac{V_{\max}}{K_m}$$

A plot of $\frac{1}{t} \ln \frac{C_{S0}}{C_S}$ vs $\frac{C_{S0} - C_S}{t}$ should be linear with slope $-\frac{1}{K_m}$

t	C _S	$\frac{C_{S0}}{C_S}$	$\frac{1}{t} \ln \frac{C_{S0}}{C_S}$	C _{S0} - C _S	$\frac{C_{S0} - C_S}{t}$
0	.0200	1.0	-	.0000	-
10	.01775	1.1268	.01193	.00225	.000225
20	.0158	1.2654	.01179	.0042	.00021
50	.0106	1.8867	.01270	.0094	.000188
100	.0050	4.0000	.01386	.0150	.00015



$$\text{From the graph, slope} = \frac{.013 - .012}{(17.5 - 20.6) \times 10^{-5}} \left(\frac{\text{min}^{-1}}{\text{g mol l min}^{-1}} \right)$$

$$= \frac{-.001}{-.31 \times 10^{-5}} \left(\frac{\text{l}}{\text{g mol}} \right) = \frac{1}{k_m}$$

$$K_m = .0310 \text{ g mol / l}$$

$$\text{At } \frac{1}{t} \ln \frac{C_{S0}}{C_S} = \frac{.031}{\text{min}}, \quad \frac{C_{S0} - C_S}{t} = \frac{1.75 \times 10^{-4}}{\text{l-min}} \frac{\text{g mol}}{\text{g mol}}$$

$$\therefore \frac{V_{\max}}{K_m} = \frac{1}{t} \ln \frac{C_{S0}}{C_S} + \frac{C_{S0} - C_S}{K_m t} = .013 \text{ min}^{-1} + \frac{1.75 \times 10^{-4}}{.0310} \frac{\text{g mol/l-min}}{\text{g mol/l}}$$

$$\frac{V_{\max}}{K_m} = (.013 + 5.64 \times 10^{-3}) \text{ min}^{-1} = .01865 \text{ min}^{-1}$$

$$V_{\max} = (.01865 \times \text{min}^{-1}) \left(.0310 \frac{\text{g mol}}{\text{l}} \right) = 5.78 \times 10^{-4} \frac{\text{g mol}}{\text{l-min}}$$

(b) $V_{\max} \propto [E]$. If the enzyme concentration is increased by a factor of three, then

$$V_{\max} = 3 \left(5.78 \times 10^{-4} \frac{\text{g mol}}{\text{l} \cdot \text{min}} \right) = 17.34 \times 10^{-4} \frac{\text{g mol}}{\text{L} \cdot \text{min}}$$

$$k_m \ln \frac{C_S}{C_{S0}} + C_S - C_{S0} = -17.34 \times 10^{-4} \frac{\text{g mol}}{\text{L} \cdot \text{min}} * 20 \text{ min} = -34.7 \times 10^{-4} \frac{\text{g mol}}{\text{L}}$$

This equation should be solved by trial and error. Rearranging,

$$\ln \frac{C_S}{C_{S0}} = \frac{C_{S0} - C_S - .0347}{K_m}$$

$$\therefore C_S = C_{S0} \exp \left[\frac{C_{S0} - C_S - .0347}{K_m} \right] = .02 \exp \left[\frac{-.0147 - C_S}{.0310} \right]$$

Assume a C_S , calculate a new one from the RHS of the above equation.

Assume C_S	New C_S	% difference
0.015	0.0077	94.8
0.0077	0.0097	20.6
0.0097	0.0091	6.6
0.0091	0.0093	2.2
0.0093	0.0092	1.1
0.0092	0.0092	0

$$C_S = 0.0092$$

P7-12



Assuming (1) and (2) to be equilibrium steps:

$$k_m = \frac{[E][S]}{[E \cdot S]} \quad (4)$$

$$k_i = \frac{[E][I]}{[E \cdot I]} \quad (5)$$

$$\text{Rate of production formation: } r_p = k_s [E \cdot S] \quad (6)$$

$$\text{Combining (4) and (6): } r_p = \frac{k_s [E][S]}{k_m} \quad (7)$$

$$\text{Total enzyme balance: } [E_0] = [E] + [E \cdot S] + [E \cdot I] \quad (8)$$

$$\text{From (4), (5), and (8): } [E_0] = [E] + \frac{[E][S]}{k_m} + \frac{[E][I]}{k_i} \quad (9)$$

$$[E] = \frac{[E_0]}{1 + \frac{[S]}{k_m} + \frac{[I]}{k_i}} \quad (10)$$

Equations (7) and (10) can be combined to give:

$$r_p = \frac{k_s [E_0][S]}{k_m + [S] + \frac{k_m}{k_i}[I]} \quad (11)$$

$$\text{Let } V_{\max} = k_s [E_0] \quad r_p = \frac{V_{\max} [S]}{[S] + k_m \left[1 + \frac{[I]}{k_i} \right]}$$

(b) Uncompetitive Inhibition





Assuming (1) and (2) to be equilibrium steps:

$$k_m = \frac{[E][S]}{[E \cdot S]} \quad (4)$$

$$k_i = \frac{[I][E \cdot S]}{[I \cdot E \cdot S]} \quad (5)$$

$$r_p = k_s [E \cdot S] \quad (6)$$

$$\text{From (4) and (6): } r_p = \frac{k_s}{k_m} [E][S] \quad (7)$$

$$\text{Total enzyme balance: } [E_0] = [E] + [E \cdot S] + [I \cdot E \cdot S] \quad (8)$$

$$\text{From (4), (5), and (8): } [E_0] = [E] + \frac{[E][S]}{k_m} + \frac{[I][E][S]}{k_i k_m} \quad (9)$$

$$\therefore [E] = \frac{[E_0]}{1 + \frac{[S]}{k_m} + \frac{[I][S]}{k_i k_m}} \quad (10)$$

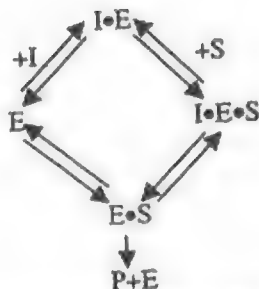
From (7) and (10) we get:

$$r_p = \frac{k_s [E_0][S]}{k_m + [S] + \frac{[I][S]}{k_i}} \quad (11)$$

$$\text{Let } k_s [E_0] = V_{\max}$$

$$r_p = \frac{V_{\max} [S]}{k_m + [S] \left[1 + \frac{[I]}{k_i} \right]} \quad (12)$$

(c) Non-competitive Inhibition



Assuming all of the reversible reactions to be equilibrium steps. The inhibitor "I", and the substrate "S" bind at different sites of the enzyme.

$$K_m = \frac{[E][S]}{[E \cdot S]} = \frac{[I \cdot E][S]}{[I \cdot E \cdot S]} \quad (1)$$

$$K_i = \frac{[E][I]}{[E \cdot I]} = \frac{[E \cdot S][I]}{[E \cdot I \cdot S]} \quad (2)$$

$$r_p = k_s [E \cdot S] \quad (3)$$

$$\text{From (1) and (3): } r_p = \frac{k_s [E \cdot S]}{K_m} \quad (4)$$

$$\text{Total enzyme balance: } [E_0] = [E] + [E \cdot S] + [I \cdot E] + [I \cdot E \cdot S] \quad (5)$$

$$[E_0] = [E] + \frac{[E][S]}{K_m} + \frac{[I][E]}{K_i} + \frac{[I][E][S]}{K_m K_i} \quad (6)$$

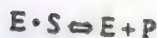
From equations (4) and (6) combined give:

$$r_p = \frac{k_s [E_0][S]}{K_m + [S] + \frac{[I] K_m [I][S]}{K_i}}$$

$$\text{Let } k_s [E_0] = V_{\max}$$

$$r_p = \frac{V_{\max} [S]}{(K_m + [S]) \left(1 + \frac{[I]}{K_i} \right)}$$

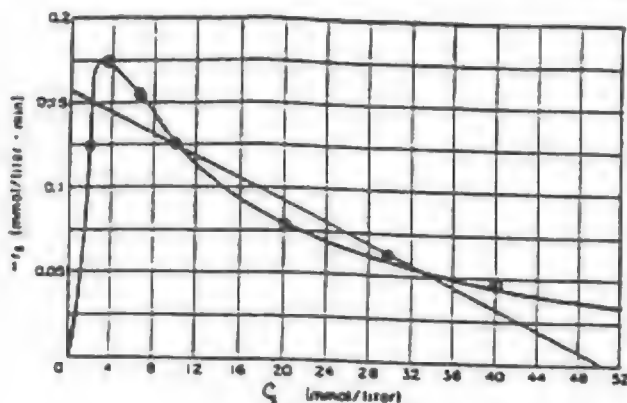
P7-13 Given the reaction sequence:



The plot of $-r_s$ vs C_s is shown below.

From problem P7-15, the mechanism for the above reaction is:

$-r_s = \frac{k C_s E_t}{1 + K_1 C_s + K_2 C_s^2}$; For $C_s \ll 1$: $-r_s = k C_s E_t$ in qualitative agreement with the graph at low values of C_s . For $C_s \gg 1$: $-r_s = \frac{k E_t}{K_2 C_s}$. This is also in agreement with the graph.



$$At \frac{\partial(-r_s)}{\partial C_s} = \frac{k E_t}{1 + K_1 C_s + K_2 C_s^2} \cdot \frac{k C_s E_t [K_1 + 2K_2 C_s]}{(1 + K_1 C_s + K_2 C_s^2)^2} = \frac{k E_t (1 - K_2 C_s^2)}{(1 + K_1 C_s + K_2 C_s^2)^2} = 0$$

$$\text{or } C_s^2 = \frac{1}{K_2} \text{ with: } \frac{\partial^2(-r_s)}{\partial C_s^2} = \frac{-2k E_t C_s K_2}{(1 + K_1 C_s + K_2 C_s^2)^2} - \frac{2k E_t (1 - K_2 C_s^2)(K_1 + 2K_2 C_s)}{(1 + K_1 C_s + K_2 C_s^2)^3}$$

$$\frac{\partial^2(-r_s)}{\partial C_s^2} = \frac{2k E_t [-3K_2 C_s - K_1 + K_2 C_s^2]}{(1 + K_1 C_s + K_2 C_s^2)^3} \text{ with } C_s^2 = \frac{1}{K_2}, \text{ the numerator becomes}$$

$$2k E_t \left[-K_1 - 3\sqrt{K_2} + \frac{1}{\sqrt{K_2}} \right] < 0 \therefore (-r_s) \text{ goes through a maximum.}$$

This observation also agrees with the above graph

(b) For a CSTR operating with $V = 1000 \text{ l}$; $u_0 = 3.2 \text{ l/min}$

$$u_0 [C_{A0} - C_A] = -r_A V \text{ or } -r_A = \frac{C_{A0} - C_A}{\tau}; \tau = \frac{V}{u_0} = \frac{1000}{3.2} = 313 \text{ min.}$$

with $C_{A0} = 50 \text{ m moles/l}$, $-r_A = \frac{50 - C_A}{313}$; this (linear) equation is plotted on the accompanying graph, the equation intersects the $(-r_s)$ vs C_s curve from the rate of reaction at

$$C_s = 34 \frac{\text{m moles}}{\text{l}}, -r_s = 0.052 \frac{\text{m moles}}{\text{min} \cdot \text{l}}, C_s = 9.4 \frac{\text{m moles}}{\text{l}},$$

$$-r_s = 0.132 \frac{\text{m moles}}{\text{min} \cdot \text{l}}, C_s = 2.1 \frac{\text{m moles}}{\text{l}}, -r_s = 0.154 \frac{\text{m moles}}{\text{min} \cdot \text{l}}.$$

Stability of points: assume that a perturbation $\theta_s = C_{s0} - \bar{C}_s$ occurs where the overbar designates the steady-state condition. Material balance for any time:

$$V \frac{dC_s}{dt} = r_s V + C_{s0} u_0 - C_s u_0$$

$$\text{or } \tau \frac{dC_s}{dt} = r_s \tau + C_{s0} - C_s$$

at steady state

$$0 = \bar{r}_s \tau + \bar{C}_{s0} - \bar{C}_s$$

Combining

$$\tau \frac{d\theta_s}{dt} = (r_s - \bar{r}_s) \tau + \theta_{s0} - \theta_s$$

Using a Taylor series expansion about \bar{C}_s to linearize $r_s - \bar{r}_s$:

$$r_s - \bar{r}_s = \left(\frac{\partial r_s}{\partial C_s} \right)_{\bar{C}_s} (C_s - \bar{C}_s) = \left(\frac{\partial r_s}{\partial C_s} \right)_{\bar{C}_s} \theta_s \text{ and substituting}$$

$$\tau \frac{d\theta_s}{dt} = \left[\left(\frac{\partial r_s}{\partial C_s} \right)_{\bar{C}_s} \tau - 1 \right] \theta_s + \theta_{s0} \text{ at } t = 0, \theta_s = 0$$

For this solution of the above equation to be stable:

$$\left(\frac{\partial r_s}{\partial C_s} \right)_{\bar{C}_s} \tau - 1 < 0 \text{ or } \left(\frac{\partial r_s}{\partial C_s} \right)_{\bar{C}_s} \tau < 1 \text{ or } \left(\frac{\partial r_s}{\partial C_s} \right)_{\bar{C}_s} \tau > -1$$

P7-13 (cont'd)

At $C_s = 2.1$ m moles/l, $-r_s = 0.154$ m moles/l-min, the slope of the reaction rate curve is positive. Therefore, this operating point is stable. For the other two points, the stability may be examined by estimating the derivative graphically:

$$\text{At } C_s = 9.4 \text{ m moles/l, } \left(\frac{\partial(-r_s)}{\partial C_s} \right)_{C_s=9.4} \equiv \frac{\Delta(-r_s)}{\Delta C_s} = \frac{0.1425 - 0.1275}{8-10} = -\frac{0.150}{2} \text{ min}^{-1}$$

$$\left(\frac{\partial(-r_s)}{\partial C_s} \right)_{C_s} \tau = \left(-\frac{0.150}{2} \text{ min}^{-1} \right) (313 \text{ min}) = -2.4 < -1$$

\therefore the point $C_s = 9.4$, $-r_s = 0.132$ is unstable.

$$\text{At } C_s = 2.1 \text{ m moles/l, } \left(\frac{\partial(-r_s)}{\partial C_s} \right)_{C_s=2.1} \equiv \frac{\Delta(-r_s)}{\Delta C_s} = \frac{0.0675 - 0.018}{24-44} = -\frac{0.0495}{20} \text{ min}^{-1}$$

$$\left(\frac{\partial(-r_s)}{\partial C_s} \right)_{C_s} \tau = \left(-\frac{0.0495}{2} \text{ min}^{-1} \right) (313 \text{ min}) = -0.775 > -1 : \text{ stable}$$

At $C_s = 5.1$ m moles/l, $-r_s = 0.154$ $\frac{\text{m moles}}{\text{l} \cdot \text{min}}$ appears to be stable, but more accurate calculation of $\left(\frac{\partial(-r_s)}{\partial C_s} \right)$ is necessary to establish this conclusion definitively.

P7-14

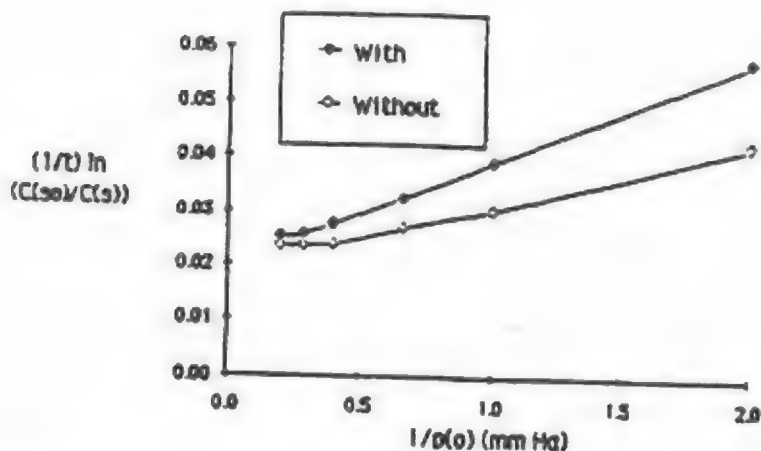
Data on Baker's Yeast at 23.4 °C

P_{O_2}	Q_{O_2} no sulfanilamide	Q_{O_2} 20 mg sulfanilamide/ml added to medium	$\frac{1}{Q_{O_2}}$ no sulfanilamide	$\frac{1}{P_{O_2}}$	$\frac{1}{Q_{O_2}}$ 20 mg sulfanilamide/ml added to medium
0.0	0.0	0.0	-	-	-
0.5	23.5	17.4	.0425	2.0	.0575
1.0	33.0	25.6	.0303	1.0	.0391
1.5	37.5	30.8	.02666	.66	.03246
2.5	42.0	36.4	.0238	.40	.02747
3.5	43.0	39.6	.0253	.285	.0253
5.0	43.0	40.0	.0233	.200	.0250

$r_p = \frac{K E_1 S}{K_m + S} = \frac{V_{max} S}{K_m + S}$, where in this problem, Q_{O_2} = oxygen uptake in microliters of O_2 per hour per mg of cells = r_p , and O_2 is the substrate.

$$\therefore \frac{1}{r_p} = \frac{K_m}{V_{max} S} + \frac{1}{V_{max}} = \frac{K_m}{V_{max}} \left(\frac{1}{P_{O_2}} \right) + \frac{1}{V_{max}} = \frac{1}{Q_{O_2}}$$

Plot of $\frac{1}{Q_{O_2}}$ versus $\frac{1}{P_{O_2}}$ will have a slope of $\frac{K_m}{V_{max}}$ and an intercept of \bar{v}_n



From the graph, slope = $\frac{0.0305 - 0.014}{1} = .0165$ Intercept = 0.019

$$\therefore V_{max} = 52.63 \frac{\text{ml } O_2}{\text{hr mg cells}}$$

$$K_m = 0.0165 V_{max} = (0.0165)(52.63) = 0.8684 \text{ mmHg}$$

(b) Now, with competitive inhibition: $E + S \rightleftharpoons E \cdot S$



$$\text{Rate law becomes: } r_p = \frac{V_{max} S}{S + K_m \left(1 + \frac{I}{K_I} \right)} \quad \text{or} \quad \frac{1}{r_p} = \frac{K_m \left(1 + \frac{I}{K_I} \right)}{V_{max}} \left(\frac{1}{S} \right) + \frac{1}{V_{max}}$$

In this case, the slope is: $\frac{K_m \left(1 + \frac{I}{K_I} \right)}{V_{max}}$ while the intercept is the same as in case (a)

P7-14 (cont'd)

For the case of uncompetitive inhibition: $E + S \rightleftharpoons E \cdot S$



Rate law becomes: $r_p = \frac{S V_{\max}}{K_m + S \left(1 + \frac{I}{K_I}\right)}$ or $\frac{1}{r_p} = \frac{K_m}{V_{\max}} \left(\frac{1}{S}\right) + \frac{1 + \frac{I}{K_I}}{V_{\max}}$

In this case, the slope is the same, but the intercept is $\frac{1 + \frac{I}{K_I}}{V_{\max}}$

And for the case of non-competitive inhibition:



$$r_p = \frac{V_{\max} S}{(S + K_m) \left(1 + \frac{I}{K_I}\right)} \quad \text{or} \quad \frac{1}{r_p} = \frac{1 + \frac{I}{K_I}}{V_{\max}} + \frac{1 + \frac{I}{K_I}}{V_{\max}} \left(\frac{1}{S}\right)$$

In this case both the slope and intercept change. Plotting the data of $\frac{1}{p_{O_2}}$ in mmHg versus $\frac{1}{Q_{O_2}}$ with sulfanilamide on the same plot as was plotted the data for the case with no sulfanilamide, it is seen that the slopes are different, but the intercept is the same. Therefore the inhibition is comparative.

P7-15

(a) No solution will be given.

(b)

$$y_j = (1-p)p^{j-1} \quad w_j = j(1-p)^2 p^{j-1}$$

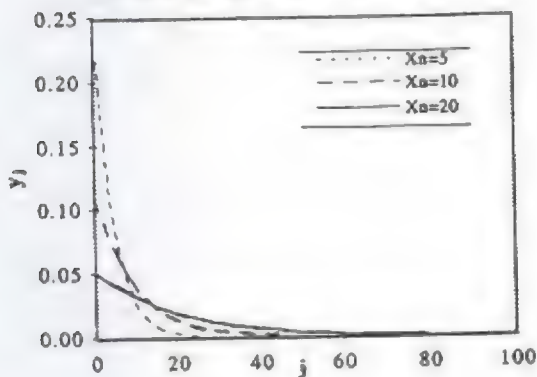
$$X_a = \frac{1}{1-p} \quad \text{For } X_a = 5: \quad p = 0.80$$

$$X_a = 10: \quad p = 0.90$$

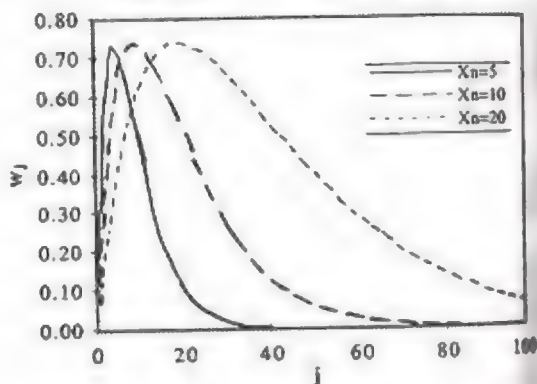
$$X_a = 20: \quad p = 0.95$$

Use these equations to generate the desired graphs:

y_j vs. j for $X_n = 5, 10, \text{ and } 20$



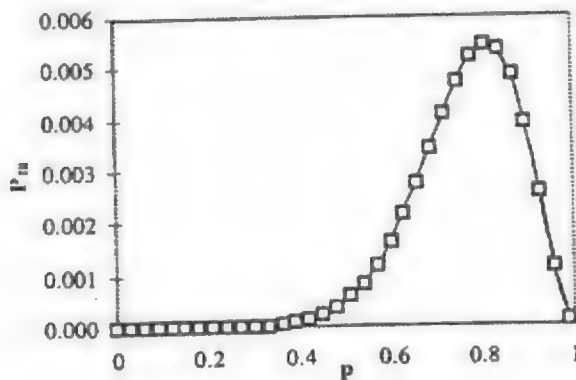
w_j vs. j for $X_n = 5, 10, \text{ and } 20$



$$P_j = M_0(1-p)^2 p^{j-1} = M_0(1-p)^2 p^9$$

Use the above equation to generate a graph of P_{10} vs. p :

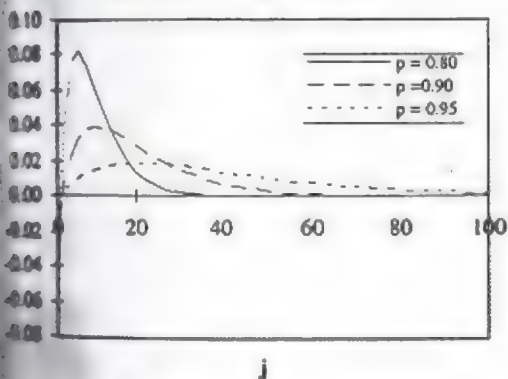
P_{10} vs. p



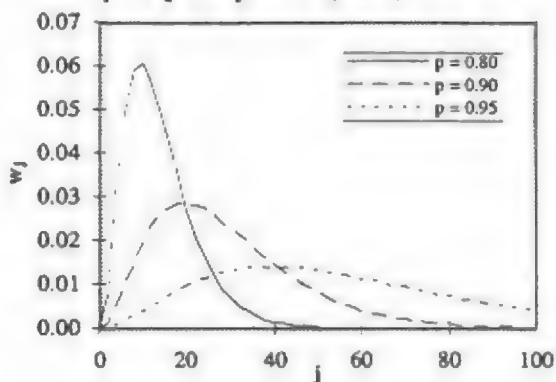
(c) $y_j = (j-1)(1-p)^2 p^{j-2}$ $w_j = \frac{1}{2} j(1-p)^3 (j-1) p^{j-2}$

Use these equations to generate graphs of y_j and w_j vs. j .

y_j vs. j for $p = 0.80, 0.90$, and 0.95



w_j vs. j for $p = 0.80, 0.90, 0.95$



(d)

$$\bar{M}_n = \mu_n M_M = \frac{M_M}{1-p}$$

$$\bar{M}_w = \mu_w M_M = M_M \frac{1+p}{1-p}$$

$$D = \frac{\mu_w}{\mu_n} = \left(\frac{1+p}{1-p} \right) (1-p) = 1+p$$

We must find the value of p .

$$\ln \frac{M}{M_0} = \left(\frac{8k_p^2 f I_{20}}{k_o k_t} \right)^{1/2} \left[\exp \left(\frac{-k_o t}{2} \right) - 1 \right] = -0.067$$

$$M = 2.803$$

$$I_2 = I_{20} \exp(-k_o t) = (0.001) \exp[(-1.4 \times 10^{-3})(14,400)] = 2.794 \times 10^{-9}$$

$$p = \beta = \frac{k_p M}{k_p M + k_m M + k_c C + k_s S + \sqrt{2k_t k_o f(I_2)}} = 0.99991$$

This can then be used to calculate the desired values:

$$\bar{M}_n = \frac{104}{1-0.99991} = 1.155 \times 10^6$$

$$\bar{M}_w = 104 \frac{(1+0.99991)}{(1-0.99991)} = 2.311 \times 10^6$$

$$D = 1+p = 1.99991$$

P7-15 (cont'd)

(c) Mole fraction of polystyrene of chain length 10 (y_{10}).

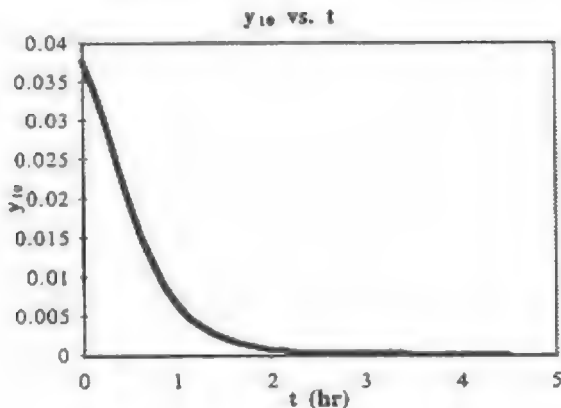
$$I_2 = I_{20} \exp(-k_o t)$$

$$M = M_o \exp \left[\left(\frac{8k_p^2 f I_{20}}{k_o k_t} \right)^{1/2} \left(\exp \left(\frac{-k_o t}{2} \right) - 1 \right) \right]$$

$$p = \beta = \frac{k_p M}{k_p M + k_{tr} M + k_t S + \sqrt{2k_t k_o f (I_2)}}$$

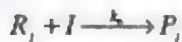
$$y_n = (1-p)p^{n-1} \quad n = 10$$

Use the above equations to plot y_n vs. t :



P7-16

Reaction



(a) and (b)

$$\bar{X}_N = \frac{-r_M}{\sum r_j} = \left(\frac{\sum r_j}{-r_M} \right)^{-1}$$

$$\sum r_j = r_i + \sum (k_p M (R_j - R_{j-1}) + (k_s + k_d) R_j + \sum R_j k_{tr} M R_j + k_t C R_j + k_s S R_j + k_n I R_j)$$

$$\text{Let } \sum R_j = R^*$$

$$\sum r_j = r_i + R^* (k_{tr} M + k_s S + k_n I)$$

P7-16 (cont'd)

$$\bar{X}_N = \left[\frac{r_i + R^* (k_m M + k_s S + k_a I)}{k_p M R^*} \right]^{-1} = \left[\frac{r_i}{-r_M} + \frac{k_m}{k_p} + \frac{k_s S}{k_p M} + \frac{k_a I}{k_p M} \right]^{-1}$$

$$\bar{X}_N = \left[\frac{r_i}{r_p} + \frac{k_m}{k_p} + \frac{k_s S}{k_p M} + \frac{k_a I}{k_p M} \right]^{-1} = \left[\left(\frac{fk_o k_i}{k_p^2} \right)^{\frac{1}{2}} \frac{I_2^{\frac{1}{2}}}{M} + \frac{k_m}{k_p} + \frac{k_s S}{k_p M} + \frac{k_a I}{k_p M} \right]^{-1}$$

- (c) From the above derivation we know that

$$\frac{1}{\bar{X}_N} = \frac{r_i}{r_p} + \frac{k_m}{k_p} + \frac{k_s S}{k_p M} + \frac{k_a I}{k_p M}$$

Neglecting the solvent term and rearranging yields:

$$\frac{1}{\bar{X}_N} = \frac{r_i}{-r_M} + \frac{k_m}{k_p} + \frac{k_a I}{k_p M} = \frac{r_i (-r_M)}{(-r_M)^2} + \frac{k_m}{k_p} + \frac{k_a I}{k_p M}$$

Substituting in for $-r_M$ and r_i and simplifying:

$$\begin{aligned} \frac{1}{\bar{X}_N} &= \frac{2k_o f(I_2)/M(-r_M)}{k_p^2 (2k_o f(I_2)/k_i)} + \frac{k_m}{k_p} + \frac{k_a I}{k_p M} \\ \frac{1}{\bar{X}_N} &= \frac{k_i (-r_M)}{k_p^2 (M)} + \frac{k_m}{k_p} + \frac{k_a I}{k_p M} \end{aligned}$$

- (d) To determine rate law parameters experimentally from a CSTR both the final X_N value and the final concentrations of M and I must be recorded. These data can be used in the above equation to find values for the parameters.
- (e) An increase in temperature would cause an increase in all three primary steps of free-radical polymerization (initiation, propagation, and termination). By looking at the overall rate law:

$$r_M = k_p M \sqrt{\frac{2k_o (I_2) f}{k_i}}$$

it can be seen that the greatest effect of temperature would be on propagation.

Overall, there would be an increase in monomer disappearance and an increase in polymerization.

P7-17

a) PFR:

$$\frac{dM}{d\tau} = r_M$$

$$\frac{dI_2}{d\tau} = r_{I_2}$$

$$r_M = -k_p M \sqrt{\frac{2k_o I_2 f}{k_t}}$$

$$r_{I_2} = -k_o I_2$$

Plug those into POLYMATH to get this graph.

Equations:

$$d(m)/d(\tau) = r_m$$

$$d(i)/d(\tau) = r_i$$

$$k_p = 10$$

$$k_o = 1e-3$$

$$f = .5$$

$$k_t = 5e7$$

$$r_i = -k_o \cdot i$$

$$r_m = -k_p \cdot m \cdot \sqrt{2 \cdot k_o \cdot i \cdot f / k_t}$$

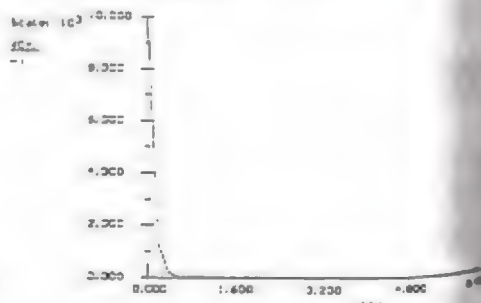
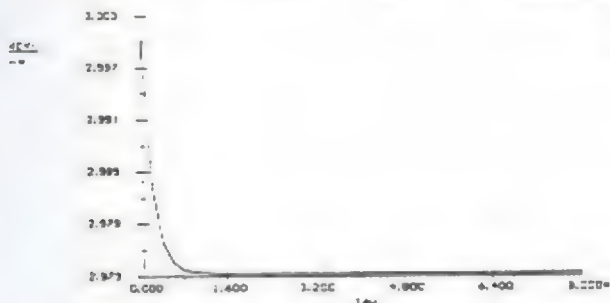
$$\tau_{a0} = 0, \quad \tau_{af} = 79998$$

Initial value

3

0.01

Variable	Initial value	Maximum value	Minimum value	Final value
tau	0	79998	0	79998
m	3	3	2.97329	2.97329
i	0.01	0.01	5.06171e-38	5.06171e-38
kp	10	10	10	10
ko	0.001	0.001	0.001	0.001
f	0.5	0.5	0.5	0.5
kt	5e+07	5e+07	5e+07	5e+07
ri	-1e-05	-5.06171e-41	-1e-05	-5.06171e-41
rm	-1.34164e-05	-2.99158e-23	-1.34164e-05	-2.99158e-23



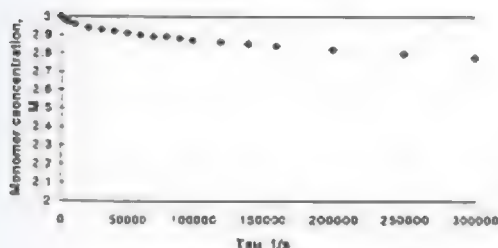
CSTR:

$$M_0 - M = -r_M \cdot \tau$$

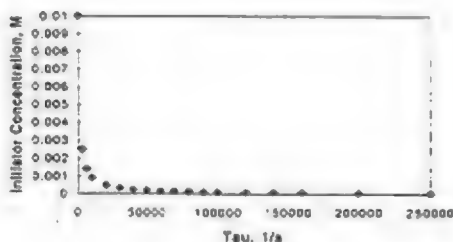
$$I_{20} - I_2 = -r_{I_2} \cdot \tau$$

The rate laws are the same so again using POLYMATH the following graphs are generated.

Monomer vs space time CSTR



Initiator Concentration vs Space Time CSTR



p7-17 cont'd

Equations:

$$f(m) = m - m_0 - r_m \cdot \tau$$

$$f(i) = i - i_0 - r_i \cdot \tau$$

$$m_0 = 3$$

$$\tau = 5e11$$

$$i_0 = .01$$

$$k_p = 10$$

$$k_0 = 1e-3$$

$$f = .5$$

$$k_t = 5e7$$

$$r_i = -k_0 \cdot i$$

$$r_m = -k_p \cdot m \cdot \sqrt{2 \cdot k_0 \cdot i \cdot f / k_t}$$

Initial value

2.5

0.001

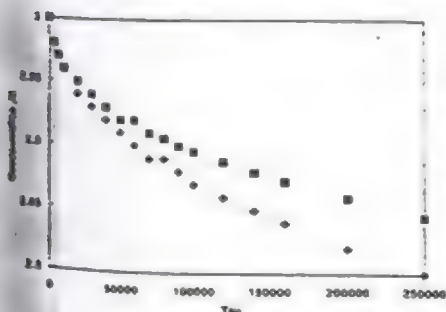
b) For two CSTRs, the design equations change just a bit.

$$M_0 - M_1 = -r_{M_1} \cdot \frac{\tau}{2} \quad I_{20} - I_{21} = -r_{I_1} \cdot \frac{\tau}{2}$$

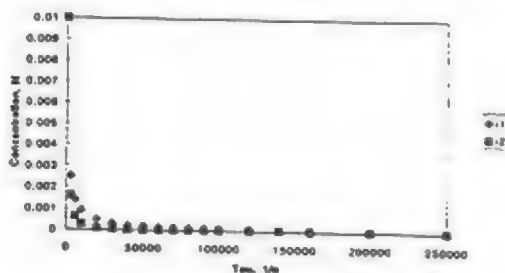
$$M_1 - M_2 = -r_{M_2} \cdot \frac{\tau}{2} \quad I_{21} - I_{22} = -r_{I_2} \cdot \frac{\tau}{2}$$

The rate laws are the same with the exception that instead of just I_2 or M , I_{21} , I_{22} , M_1 , or M_2 are used depending on which reactor they came from and the following graphs are generated.

One CSTR vs Two CSTRs



One CSTR vs Two CSTRs



c) Making k_0 bigger causes I_2 to decrease rapidly and M does not get formed as much. Increasing k_p causes M to decrease slightly, but not by that much. Increasing k_t causes M not to decrease by very much staying very close to 3.

p7-18 No solution will be given

$$I + M \xrightarrow{k_i} R_1$$

$$R_j + M \xrightarrow{k_p} R_{j+1}$$

$$-r_i = k_i MI$$

a) Balance on I

$$\tau = \frac{I_0 - I}{-r_i} = \frac{I_0 - I}{k_i MI}$$

$$\Rightarrow I = \frac{I_0}{1 + \tau k_i M}$$

$$-r_M = k_i MI + k_p M \sum_{j=1}^{\infty} R_j$$

$$\text{As } \sum_{j=1}^{\infty} R_j = I_0 - I$$

$$-r_M = k_i MI + k_p M(I_0 - I)$$

Balance on M:

$$\tau = \frac{M_0 - M}{-r_M} = \frac{M_0 - M}{k_i MI + k_p M(I_0 - I)}$$

$$\Rightarrow \tau k_i MI + \tau k_p M(I_0 - I) = M_0 - M$$

$$\Rightarrow \frac{\tau k_i M I_0}{1 + \tau k_i M} + \frac{\tau k_p I_0 M (\tau k_i M)}{1 + \tau k_i M} = M_0 - M$$

$$\Rightarrow \tau k_i I_0 M + \tau^2 k_p k_i I_0 M^2 = (M_0 - M)(1 + \tau k_i M)$$

$$\Rightarrow \tau k_i (1 + \tau k_p I_0) M^2 + (1 + \tau k_i I_0 - \tau k_i M_0) M - M_0 = 0$$

$$\Rightarrow M = \frac{-(1 + \tau k_i I_0 - \tau k_i M_0) + \sqrt{(1 + \tau k_i I_0 - \tau k_i M_0)^2 + 4 * \tau k_i (1 + \tau k_p I_0) M_0}}{2 \tau k_i (1 + \tau k_p I_0)}$$

b) $-r_{R_1} = -k_i MI + k_p MR_1$

Balance on R_1

$$\tau = \frac{0 - R_1}{-k_i MI + k_p MR_1} \Rightarrow R_1 = I \left(\frac{\tau k_i M}{1 + \tau k_p M} \right)$$

$$-r_{R_2} = -k_p MR_1 + k_p MR_2$$

Balance on R_2

$$\tau = \frac{0 - R_2}{-k_p MR_1 + k_p MR_2} \Rightarrow R_2 = R_1 \left(\frac{\tau k_p M}{1 + \tau k_p M} \right)$$

Similarly,

$$R_3 = R_2 \left(\frac{\tau k_p M}{1 + \tau k_p M} \right)$$

P7-19 cont'd

$$R_j = R_1 \left(\frac{k_p M}{1 + k_p M} \right)^{j-1}$$

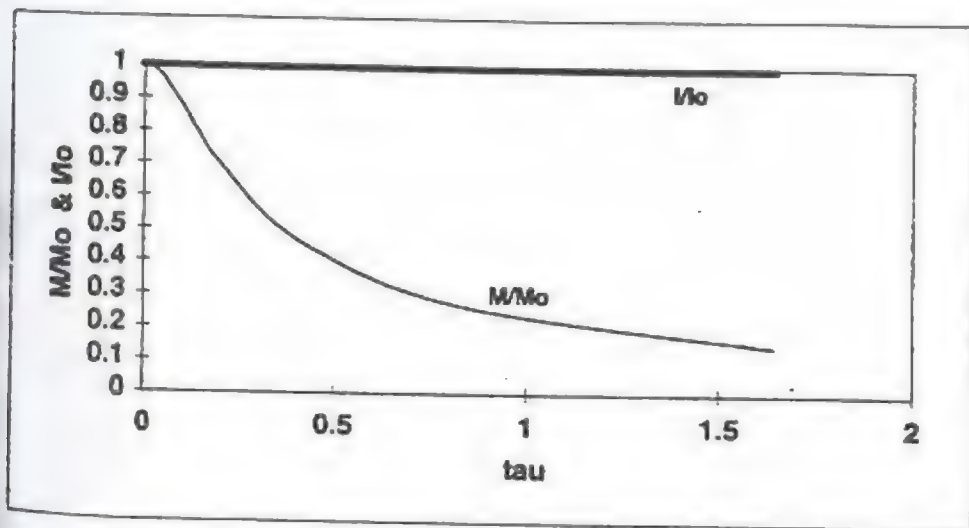
$$R_j = I \left(\frac{k_p M}{1 + k_p M} \right) \left(\frac{k_p M}{1 + k_p M} \right)^{j-1}$$

$$R_j = \frac{I(k_p M)}{k_p M} \left(\frac{k_p M}{1 + k_p M} \right)^j$$

$$R_j = \frac{I_0}{1 + k_p M} \frac{k_i}{k_p} \left(\frac{k_p M}{1 + k_p M} \right)^j$$

c) Initiation Rate constant $k_i \ll k_p$ propagation rate constant
Hence, nearly no change in the concentration of Initiator (I).

Mo	1
Io	1
ki	0.015
kp	1000



d)

$$\lambda_0 = \sum_{j=1}^{\infty} R_j = I_0 - I = \frac{k_i M I_0}{1 + k_p M}$$

$$\lambda_1 = \sum_{j=1}^{\infty} j R_j = \frac{I_0}{1 + k_p M} \frac{k_i}{k_p} \sum_{j=1}^{\infty} j \left(\frac{k_p M}{1 + k_p M} \right)^j$$

$$= \frac{I_0}{1 + \tau k_i M} \frac{k_i}{k_p} \left[\frac{\tau k_p M / (1 + \tau k_p M)}{\left[1 - \frac{\tau k_p M}{(1 + \tau k_p M)} \right]^2} \right]$$

$$\text{As } \sum_{j=1}^{\infty} j x^j = \frac{x}{(1-x)^2}$$

$$\lambda_1 = \frac{\tau k_i M I_0}{1 + \tau k_i M} (1 + k_p M)$$

$$\lambda_2 = \sum_{j=1}^{\infty} j^2 R_j = \frac{I_0}{1 + \tau k_i M} \frac{k_i}{k_p} \sum_{j=1}^{\infty} j^2 \left(\frac{\tau k_p M}{1 + \tau k_p M} \right)^j$$

$$= \frac{I_0}{1 + \tau k_i M} \frac{k_i}{k_p} \left[\frac{\left(\frac{\tau k_p M}{1 + \tau k_p M} \right) \left(1 + \frac{\tau k_p M}{1 + \tau k_p M} \right)}{\left(1 - \frac{\tau k_p M}{1 + \tau k_p M} \right)^3} \right]$$

$$\text{As } \sum_{j=1}^{\infty} j^2 x^j = \frac{x(1+x)}{(1-x)^3}$$

$$\Rightarrow \lambda_2 = \frac{\tau k_i M I_0}{1 + \tau k_i M} (1 + \tau k_p M) (1 + 2\tau k_p M)$$

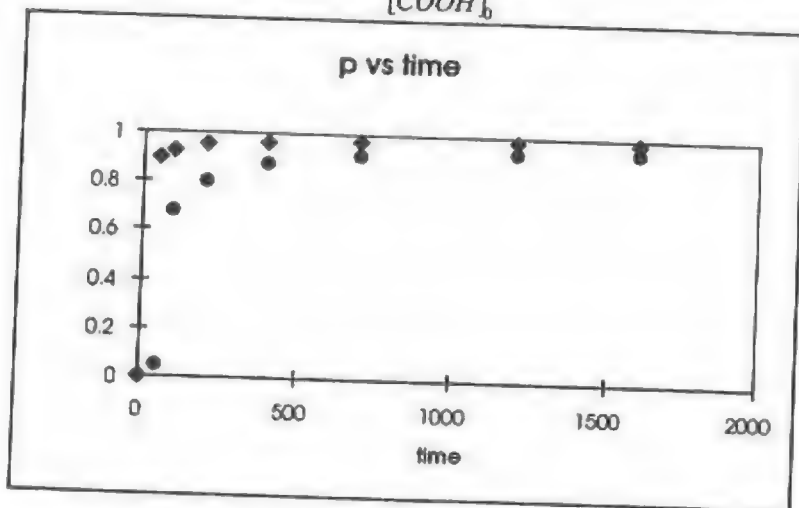
$$\boxed{\begin{aligned} \mu_s &= \frac{\lambda_1}{\lambda_0} = (1 + \tau k_p M) \\ \mu_w &= \frac{\lambda_2}{\lambda_1} = (1 + 2\tau k_p M) \\ D &= \frac{\mu_w}{\mu_s} = \frac{1 + 2\tau k_p M}{1 + \tau k_p M} \end{aligned}}$$

a) With the reaction self catalyzed the mole balance and rate law becomes:

$$-\frac{d[\text{COOH}]}{dt} = k[\text{COOH}]^3$$

We can then get $[\text{COOH}]$ as a function of time. The following graph shows both the given values of p and the calculated value as a function of time where

$$p = \frac{[\text{COOH}]_p - [\text{COOH}]_b}{[\text{COOH}]_b}$$



It appears to follow this above 500 min.

b) The new mole balance and rate law is:

$$-\frac{d[\text{COOH}]}{dt} = k[\text{COOH}][\text{OH}][\text{H}^+]$$

$$[\text{OH}] = [\text{COOH}]$$



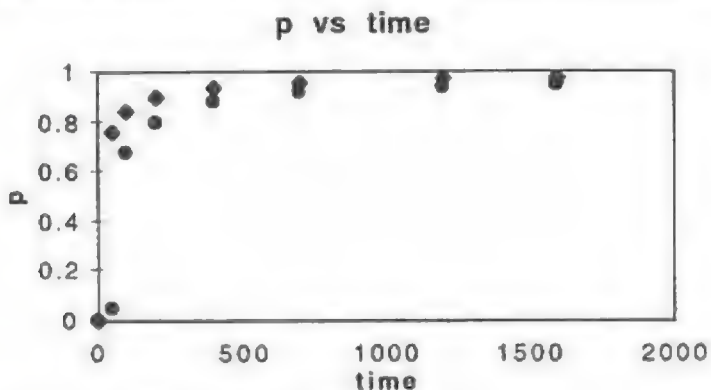
$$K_{eq} = \frac{[\text{COO}^-][\text{H}^+]}{[\text{COOH}]}$$

$$[\text{COO}^-] = [\text{H}^+]$$

$$[\text{H}^+]^2 = K_{eq}[\text{COOH}]$$

$$-\frac{d[\text{COOH}]}{dt} = k[\text{COOH}]^{\frac{3}{2}}$$

Solving for $[\text{COOH}]$ as a function of time gives the following graph:



It follows the data above 200 min.

- c) This mechanism can be made to fit either rate law, depending on whether HA dissociates before or after the first reaction.

P7-21 No solution will be given

$$I + M \xrightarrow{k_0} R_1$$

$$R_j + M \xrightarrow{k_p} R_{j+1}$$

$$-\frac{dI}{dt} = k_0 MI = (k_p M) \frac{k_0 I}{k_p}$$

$$-\frac{dI}{k_p M dt} = \frac{k_0}{k_p} I$$

$$d\theta = k_p M dt$$

$$\frac{dI}{d\theta} = -\frac{k_0}{k_p} I \Rightarrow I = I_0 e^{-\frac{k_0 \theta}{k_p}}$$

$$-\frac{dR_1}{dt} = -k_0 MI + k_p MR_1$$

$$\frac{dR_1}{d\theta} = \frac{k_0}{k_p} I_0 e^{-\left(\frac{k_0}{k_p}\right)\theta} - R_1$$

$$\frac{d(e^{\theta} R_1)}{d\theta} = \frac{k_0}{k_p} I_0 e^{-\left(\frac{k_0}{k_p}\right)\theta}$$

$$\Rightarrow R_1 = \frac{k_0}{k_p} \frac{I}{\left(1 - \frac{k_0}{k_p}\right)} \left[e^{-\frac{k_0 \theta}{k_p}} - e^{-\theta} \right]$$

$$-\frac{dR_2}{dt} = -k_p MR_1 + k_p MR_2$$

$$\Rightarrow \frac{dR_2}{d\theta} = R_1 - R_2$$

$$\Rightarrow \frac{d(e^{\theta} R_2)}{d\theta} = e^{\theta} R_1 = \frac{k_0 I_0}{k_p - k_0} \left[e^{\left(1 - \frac{k_0}{k_p}\right)\theta} - 1 \right]$$

$$\Rightarrow R_2 = \frac{k_0 I_0}{k_p \left(1 - \frac{k_0}{k_p}\right)^2} \left[e^{-\frac{k_0 \theta}{k_p}} - e^{-\theta} \right] - \frac{k_0 I_0 \theta e^{-\frac{k_0 \theta}{k_p}}}{k_p - k_0}$$

$$\frac{dR_j}{d\theta} = R_j - R_j$$

$$\Rightarrow \frac{d(e^\theta R_j)}{d\theta} = \frac{k_0 I_0}{k_p \left(1 - \frac{k_0}{k_p}\right)^2} \left[e^{\left(1 - \frac{k_0}{k_p}\right)\theta} - 1 \right] - \frac{k_0 I_0 \theta}{k_p \left(1 - \frac{k_0}{k_p}\right)}$$

$$\Rightarrow R_j = \frac{k_0 I_0}{k_p \left(1 - \frac{k_0}{k_p}\right)^3} \left[e^{-\frac{k_0}{k_p}\theta} - e^{-\theta} \right] - \frac{k_0 I_0}{k_p \left(1 - \frac{k_0}{k_p}\right)^2} \theta e^{-\theta} - \frac{k_0 I_0}{k_p \left(1 - \frac{k_0}{k_p}\right)^2} \frac{\theta^2 e^{-\theta}}{2}$$

$$\Rightarrow R_j = \frac{k_0 I_0}{k_p \left(1 - \frac{k_0}{k_p}\right)} \left[\frac{e^{-\frac{k_0}{k_p}\theta} - e^{-\theta}}{\left(1 - \frac{k_0}{k_p}\right)^{j-1}} - \sum_{i=1}^{j-1} \frac{\theta^i e^{-\theta}}{(i)! \left(1 - \frac{k_0}{k_p}\right)^{j-1}} \right]$$

For $j > 1$

$$I + M \xrightarrow{k_0} R_1$$

$$R_j + M \xrightarrow{k_p} R_{j+1}$$

$$\tau = \frac{I_0 - I}{k_0 M I}$$

$$\theta' = k_p M \tau$$

$$\theta' = \frac{k_p (I_0 - I)}{k_0 I}$$

$$I = \frac{k_p I_0}{k_0 \theta' + k_p}$$

$$\tau = \frac{M_0 - M}{k_p M I_0}$$

$$M = \frac{M_0}{k_p I_0 \tau + 1}$$

$$\theta' = \frac{k_p M_0 \tau}{k_p I_0 \tau + 1}$$

$$\tau = \frac{R_1}{k_0 M I - k_p M R_1}$$

$$R_1 = \frac{k_0 I \theta'}{k_p (1 + \theta')}$$

$$\tau = \frac{R_2}{k_p M R_1 - k_p M R_2}$$

$$R_2 = \frac{R_1 \theta'}{1 + \theta'} = \frac{k_0 k_p I_0 \theta'^2}{k_p (1 + \theta')^2 (k_0 \theta' + k_p)} = \frac{k_0 I_0 \theta'^2}{(1 + \theta')^2 (k_0 \theta' + k_p)}$$

$$R_j = \frac{k_0 I_0 \left(\frac{k_p M_0 \tau}{k_p I_0 \tau + 1} \right)^j}{(k_0 \theta' + k_p) \left(1 + \frac{k_p M_0 \tau}{k_p I_0 \tau + 1} \right)^j}$$

P7-24

$$(1) \quad r_g = \frac{\mu}{1 + \frac{C_C}{C_m}} C_C \quad \mu_{\max} = 0.5 \text{ hr}^{-1}$$

$$C_m = 20 \text{ g/dm}^3$$

Substrate in excess

(a) Batch reactor $V = 2 \text{ dm}^3$ (constant)

$$\frac{dC_C}{dt} = r_g \quad \frac{dC_C}{dt} = \mu_m \left(1 - \frac{C_C}{C_m} \right) C_C$$

$$\frac{dC_C}{dt} = \mu_m \left(C_C - \frac{C_C^2}{C_m} \right)$$

$$\boxed{\frac{dC_C}{dt} = 0.5 \text{ hr}^{-1} \left(C_C - \frac{C_C^2}{20 \text{ g/dm}^3} \right) \text{ plot}}$$

$$C_{C0} = \frac{0.4 \text{ g}}{2 \text{ dm}^3} = 0.2 \frac{\text{g}}{\text{dm}^3}$$

(b) $V \frac{dC_C}{dt} = F(C_{C0} - C_C) + r_g V$

$$\boxed{\frac{dC_C}{dt} = \frac{F}{V} (C_{C0} - C_C) + r_g} \quad D = \frac{F}{V}$$

$$C_{C0} = 0 \text{ (no cell injunction)}$$

$$-D C_C + r_g = 0$$

$$-D C_C + \mu C_C = 0$$

$$\therefore D = \mu$$

Wash out When $D > \mu$ or

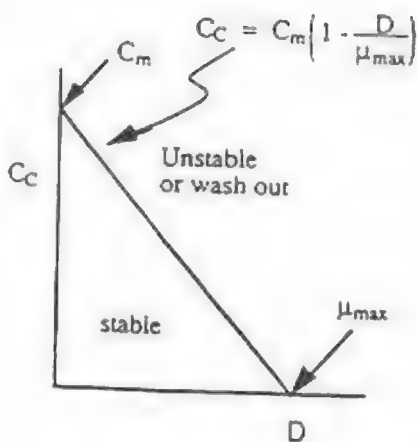
$$D > \mu_{\max} \left(1 - \frac{C_C}{C_m} \right)$$

$$\text{When } D = 0, C_C = C_m$$

$$\text{When } C_C = 0 \quad D = \mu_{\max}$$

P7-24 (cont'd)

A plot of C_C vs D gives:



(2)

Let $C = C_C$ and $K = C_m$

$$\frac{dC}{dt} = \mu C \left(1 - \frac{C}{K} \right) \quad \text{at } t = 0, C = C_0$$

$$\frac{dC}{dt} = \mu \left(C - \frac{C^2}{K} \right)$$

$$\frac{dC}{C^2 - CK} = \frac{-\mu}{K} dt \quad \frac{dC}{C(C-K)} = \frac{-\mu}{K} dt$$

$$\int_{C_0}^C \frac{dC}{C(C-K)} = \int_{C_0}^C \left(-\frac{1}{KC} + \frac{1}{K(C-K)} \right) dC$$

$$= -\frac{1}{K} \ln C + \frac{1}{K} \ln (C-K) \Big|_{C=C_0}$$

$$= \frac{1}{K} \ln \frac{C_0}{C} + \frac{1}{K} \ln \left(\frac{C-K}{C_0-K} \right)$$

$$\frac{1}{K} \ln \left(\frac{C_0(C-K)}{C(C_0-K)} \right) = \frac{-\mu}{K} t$$

$$\therefore \ln \frac{C_0(C-K)}{C(C_0-K)} = -\mu t$$

$$\frac{C_0(C-K)}{C(C_0-K)} = e^{-\mu t}$$

$$\frac{C-K}{CK} = \frac{C_0-K}{C_0 K} e^{-\mu t}$$

P7-24 (cont'd)

$$\frac{C}{CK} - \frac{K}{CK} = \left[\frac{C_0}{C_0 K} - \frac{K}{C_0 K} \right] e^{-\mu t}$$

$$\frac{1}{K} - \frac{1}{C} = \left[\frac{1}{K} - \frac{1}{C_0} \right] e^{-\mu t}$$

$$\frac{1}{C} = \frac{1}{K} + \left[\frac{1}{C_0} - \frac{1}{K} \right] e^{-\mu t}$$

$$\frac{1}{C_C} = \frac{1}{20} + \left(\frac{1}{0.2} - \frac{1}{20} \right) e^{-0.5 t}$$

$$\frac{1}{C_C} = 0.05 + 4.95 e^{-0.5 t}$$

P7-25

Run #1 No Yeast Extract
 #2 Yeast Extract

The percent volume of the growth product H_2S collected above the broth was reported as a function of time:

cell + nutrient \rightarrow more cells + product

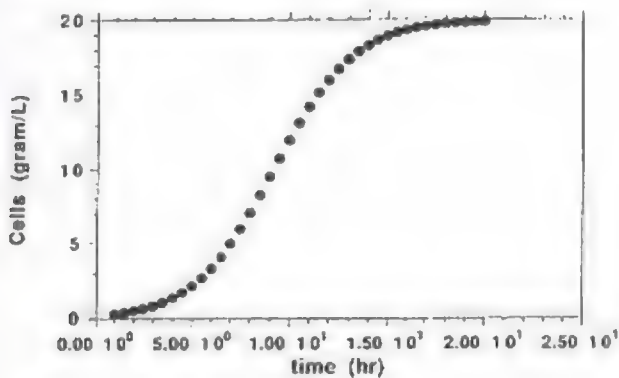
(a and b)

$$C_X = C_{X0} e^{\mu(1-t_{lag})}$$

$$\text{or } C_X = C_{X0} e^{\mu t} e^{-\mu t_{lag}}$$

curve fit exponential curve:

$$X = A e^{kt}$$



7-48

P7-25 (cont'd)

where $A = C_{X0} e^{-\mu t_{lag}}$

$$t_{lag} = \ln \frac{\left(\frac{C_{X0}}{A} \right)}{\mu}$$

Run 1 (between 15, 20, 30 hrs)

$$\mu_{max} = 0.2125 \text{ hr}^{-1}$$

$$A = 7492.6$$

$$t_{lag} = \ln \left(\frac{2.7 \times 10^4}{7492.6} \right) = 0.21252$$

$$t_{lag} = 6.0 \text{ hr}$$

Run 2 (points 10, 15, 20 hrs)

$$\mu_{max} = 0.3124 \text{ hr}^{-1}$$

$$A = 5571.7$$

$$t_{lag} = 5.1 \text{ hr}$$

(c) Stationary

$t_{stationary}$ between

Time length of time 45 to 55
10 hr

25 to 15
20 hr

(d) Product start at end of exponential (for both runs)

(e) $\frac{dC_C}{dt} = D(C_{C0} - C_C) + \mu C_C = 0$

$$D(C_{C0} - C_C) + \mu C_C = 0$$

$$C_C = 0$$

$$-D C_C + \mu C_C = 0$$

$$C_C = 0 \text{ or } D = \mu \text{ wash out occurs when } D > \mu_{max}$$

P7-26 Cell Balance

(a+b) $\frac{dC_C}{dt} = D(C_{C_{in}} - C_C) + r_s$

$$\frac{dC_C}{dt} = 0 \quad C_{C_{in}} = 0$$

$$0 = -D C_C + r_s$$

$$C_{S0} = 30$$

$$\mu_{max} = 1.5 \text{ hr}^{-1}$$

$$C_{S_{in}} = C_{C0} = 0.5 \text{ g/dm}^3$$

$$K_i = 50 \text{ g/dm}^3$$

$$K_s = 1 \text{ g/dm}^3$$

$$D = 0.75$$

$$y_{C/S} = 0.08$$

7-49

$$0 = -DC_C + \left(\frac{\mu_{\max} C_S C_C}{K_S + C_S \left(1 + \frac{C_S}{K_I} \right)} \right)$$

$$D = \left(\frac{\mu_{\max} C_S}{K_S + C_S \left(1 + \frac{C_S}{K_I} \right)} \right)$$

$$D = \left(\frac{1.5 C_S}{1 + C_S \left(1 + \frac{C_S}{8} \right)} \right)$$

$$C_S = C_{S0} - y_{S/X} C_C \quad \text{by definition}$$

$$y_{S/X} = \frac{1}{y_{S/X}} = \frac{1}{0.08} = 12.5$$

$$C_C = \frac{C_{S0} \cdot C_S}{y_{S/X}} = \frac{C_{S0}}{12.5}$$

$$D = \left(\frac{\mu_{\max} C_S}{K_S + C_S \left(1 + \frac{C_S}{K_I} \right)} \right) \quad C_C = y_{C/S} (C_{S0} - C_S)$$

pick C_S , calculate D and C_C

$$C_{S0} = 30.0 \text{ g/dm}^3$$

$$D = \left(\frac{1.5 C_S}{1 + C_S \left(1 + \frac{C_S}{8} \right)} \right)$$

$$C_C = (30.0 - C_S)(0.08)$$

(c) IN - OUT + GEN = ACC

$$\frac{dC_C}{dt} = D(C_{C_{IN}} - C_C) + r_g \quad r_g = \frac{\mu_{\max} C_S}{K_S + C_S + \left(1 + \frac{C_S}{K_I} \right) C_C}$$

$$\frac{dC_C}{dt} = D(C_{C_{IN}} - C_C) + y_{S/X} r_g$$

$$@ t = 0 \quad C_{S0} = 30$$

$$C_{C0} = 0.5$$

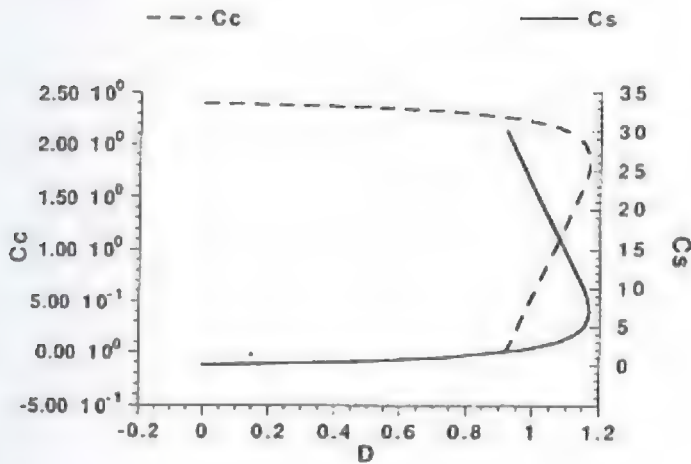
$$\text{where} \quad D = 0.75$$

$$K_I = 50$$

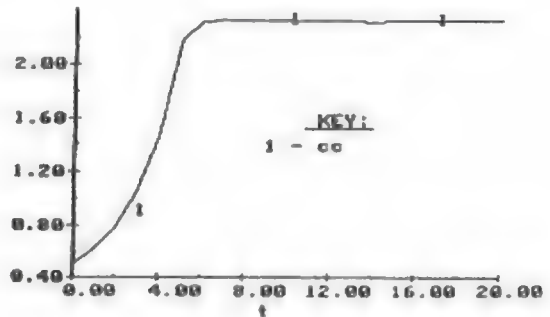
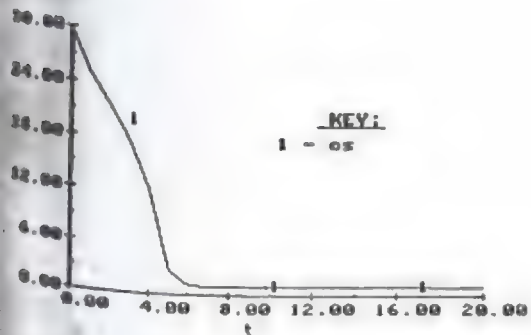
$$K_S = 1$$

$$\mu = 1.5 \quad y_{C/S} = 0.08$$

$$C_{S_{IN}} = 30$$



The equations:
 $d(cc)/d(t) = -d*cc + rg$
 $d(cs)/d(t) = d*(csin - cs) - rg/ycs$
 $ki = 50$
 $rg = 1.5*cc*cs / (1 + cs + cs*cs/ki)$
 $ycs = 0.08$
 $csin = 30$
 $d = 0.75$
 Initial values: $t_0 = 0.0$, $cc_0 = 0.5000$, $cs_0 = 30.000$
 Final value: $t_f = 20.000$



P7-27



$$\text{IN} - \text{OUT} + \text{GEN} = \text{ACC}$$

$$\frac{dN_C}{dt} = F_C + r_2 V$$

$$r_2 = k C_C$$

$$\frac{dN_C}{dt} = F_C + k C_C V$$

$$N_C = C_C V$$

$$\frac{dN_C}{dt} = F_C - k N_C$$

$$\frac{dN_C}{dt} - k N_C = F_C$$

$$N_C = \frac{-F_C}{k} + A e^{kt} \quad t = 0, N_C = 0, A = \frac{F_C}{k}$$

$$N_C = \frac{F_C}{k} [e^{kt} - 1]$$

$$C_C = \frac{N_C}{V_0 + v_0 t}$$

$$N_C = C_C (v_0 t)$$

$$F_C = C_{C0} v_0$$

$$N_C = C_C v_0 t$$

$$F_C = 0.001 \text{ gm/dm}^3 v_0$$

$$N_C = 0.025 \text{ g/dm}^3 (2 \text{ hr}) (v_0)$$

$$= 0.050 \text{ g hr/dm}^3 (v_0)$$

$$N_C = \frac{F_C}{k} [e^{kt} - 1]$$

$$1 = \frac{F_C}{N_C k} [e^{kt} - 1]$$

$$1 = \frac{C_{C0} (v_0)}{C_C (v_0) t k} [e^{kt} - 1]$$

$$1 = \frac{C_{C0} [e^{kt} - 1]}{C_C \frac{kt}{t}}$$

$$1 = \frac{0.001 \text{ gm/dm}^3 (v_0)}{0.050 \text{ g hr/dm}^3 (v_0)} \left[\frac{e^{kt} - 1}{k} \right]$$

$$k = 2.4 \text{ hr}^{-1}$$

P7-28

Plot $\log C_C$ vs t

	Slope μ	Intercept	Time range for curve fit
1	0.39218	1.172×10^7	4 to 8 hr
5	0.79507	1.7953×10^6	5 to 9 hr
10	0.75862	1.8949×10^6	4 to 10 hr
15	0.79157	1.4949×10^6	6 to 9 hr

$$\text{Slopes} = \mu [\text{hrs}]^{-1}$$

$$x = x_0 e^{\mu(t - t_{0s})}$$

$$\text{curve fit } x = A e^{\mu t}$$

$$A = e^{-\mu t_{0s}}$$

$$t_{0s} = \frac{1}{\mu} \ln \left[\frac{x_0}{A} \right]$$

7-52

	$t_{\log} [\text{hr}]$
1	2.397
5	3.23
10	3.10
15	2.80

$C_S (\text{g/l})$	$\mu (\text{hr}^{-1})$	$t_{\text{lag}} (\text{hr})$
1	.392	2.4
5	.745	3.2
10	.759	3.1
15	.792	2.8

$$\mu = \mu_{\max} \frac{C_S}{K_S + C_S}$$

$$\frac{1}{\mu} = \frac{K_S}{\mu_{\max}} \frac{1}{C_S} + \frac{1}{\mu_{\max}}$$

Curve fit data to Lineweaver-Burke Equation

$$\text{int} = 1.139 \quad \text{slope} = 1.4019$$

$$\mu_{\max} = 0.8780 \text{ hr}^{-1}$$

$$K_S = 1.23 \text{ g/l}$$

Note: curve fits assume constant nutrient concentration in batch reactor.

$$\text{b) } \frac{dC_C}{dt} = \mu C_C \left[1 - \frac{(C_C - C_{C0})}{C_{P^*}} \right]^n$$

$$\text{take } \frac{dC_C}{dt} = 0 \text{ stationary phase} \quad \text{for } n = 1$$

$$\frac{(C_C - C_{C0})}{C_{P^*}} = 1 \quad C_{P^*} = C_C - C_{C0}$$

	$C_{P^*} [X 10^7]$	$C_{C0} \text{ at } t_{\text{lag}}$	$C_C \times 10^{-7}$	Predict
1	45.73	1.172×10^7	46.9	
5	165	1.795×10^6	165	
10	256	1.895×10^6	256	3.5×10^8
15	306	1.4499×10^6	306	

	μ	t_{lag}	C_{P^*}	$C_C \text{ at } t = 0$
1	0.392	2.4	45.7×10^7	3×10^7
5	0.745	3.2	165×10^7	2×10^7
10	0.759	3.1	256×10^7	2×10^7
15	0.792	2.8	306×10^7	1.3×10^7

$$n = 1.0$$

$$r_s = \mu C_C \left[1 - \frac{C_C - C_{C \text{ at } t=0}}{C_{P^*}} \right]^n$$

$$C_{P^*} = Y_{C/S} (C_{S0}) \quad n = 1.0$$

$$Y_{C/S} = \frac{2.7 \times 10^5 \text{ cell/ml}}{\text{mg suc / L}}$$

$$r_s = \frac{dC_C}{dt}$$

7-53

The equations:

$$d(cc)/d(t) = rg$$

$$\mu = 0.792$$

$$c_0 = 1.33e7$$

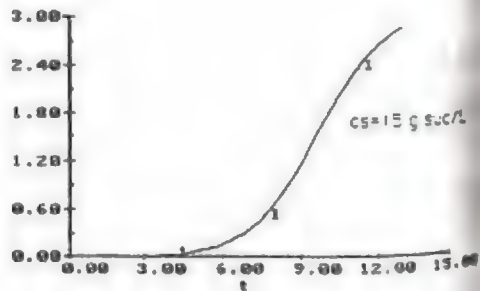
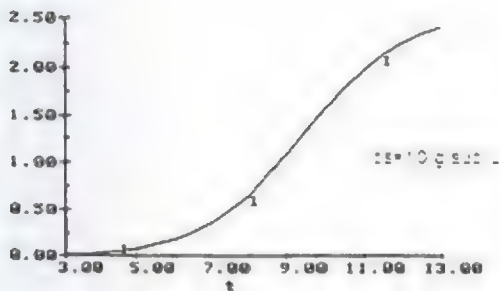
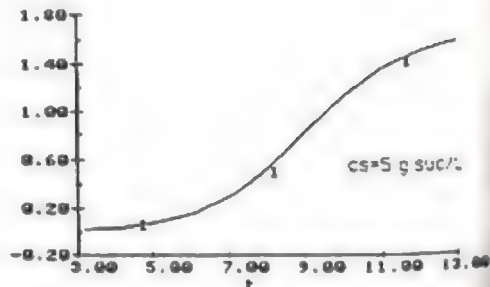
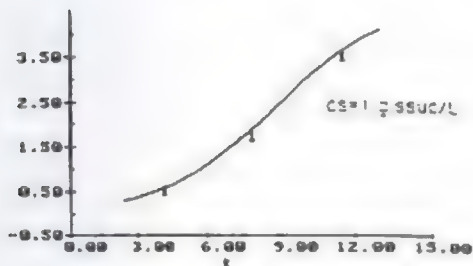
$$c_{star} = 306e7$$

$$n = 1$$

$$rg = \mu * c_0 * (1 - (cc - c_0) / c_{star}) ** n$$

Initial values: $t_0 = 2.8000$, $cc_0 = 1.330 \times 10^7$

Final value: $t_f = 13.000$



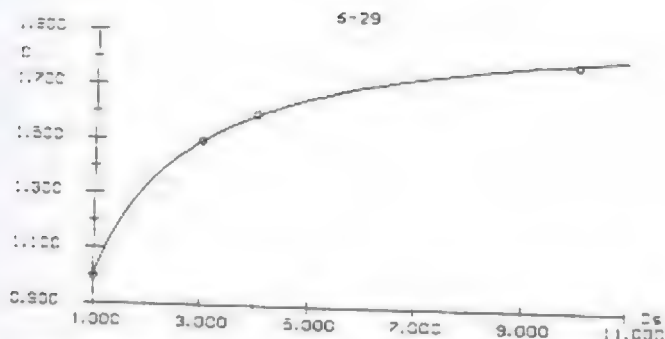
P7-29

Fit the data to the equation:

$$D = \frac{C_s \mu}{K_s + C_s}$$

Using POLYMATH, find the values for μ_{max} and K_s . They are 1.98 and 0.97 respectively.

P7-29 cont'd



- b) Using this equation, solve for Y_{CS} :

$$C_c = \frac{Y_{CS}(C_{So} + K_s)}{\mu_{\max} - D} \left(\frac{\mu_{\max} C_{So}}{K_s + C_{So}} - D \right)$$

With the given information $Y_{CS} = 0.099$, therefore, Y_{SC} is equal to the inverse of that, 10.075.

P7-30

The only equation not given is for that of the cells:

$$\frac{dC}{dt} = rg$$

$$rg = \mu C$$

We can then plug into POLYMATH and come up with the following graphs.

Equations:

$$d(p)/d(t) = (\text{alp} \cdot \mu + \text{bet}) \cdot x$$

$$d(s)/d(t) = 1/\text{yps} \cdot (\text{alp} \cdot \mu + \text{bet}) \cdot x$$

$$d(c)/d(t) = \text{rg}$$

$$\text{alp} = 34.5$$

$$\text{bet} = -.147$$

$$\text{yps} = 1.33$$

$$\mu_0 = .25$$

$$\text{ks} = .018$$

$$\text{ksi} = 11.8$$

$$\text{psta} = 32.4$$

$$\text{kpi} = .06$$

$$\text{so} = 50$$

$$x = (\text{so} - s) / \text{so}$$

$$\mu = \mu_0 \cdot (s / (\text{ks} + s + s^2 / \text{ksi})) \cdot (1 - \text{p}/\text{psta}) \cdot \exp(-\text{kpi} \cdot \text{p})$$

$$\text{rg} = \mu \cdot c$$

$$t_0 = 0, \quad t_f = 500$$

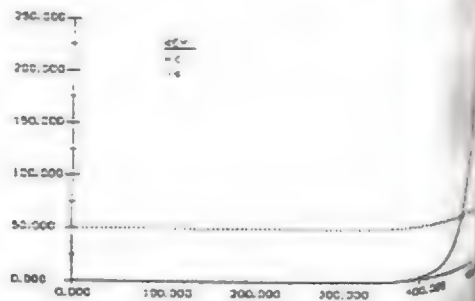
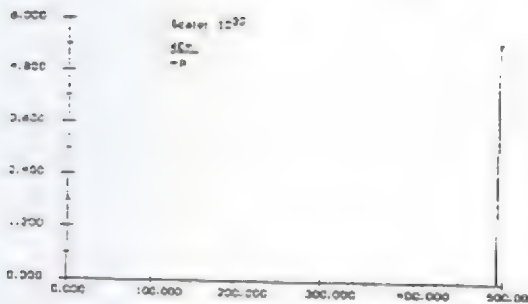
Initial value

0

50

1e-08

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	500	0	500
p	0	5.46711e-22	0	5.46711e-22
s	50	50	50	50
c	1e-08	231.597	1e-08	231.597
alp	34.5	34.5	34.5	34.5
bet	-0.147	-0.147	-0.147	-0.147
yps	1.33	1.33	1.33	1.33
mu0	0.25	0.25	0.25	0.25
ks	0.018	0.018	0.018	0.018
ksi	11.8	11.8	11.8	11.8
psta	32.4	32.4	32.4	32.4
kpi	0.06	0.06	0.06	0.06
so	50	50	50	50
x	0	0	0	0
mu	0.0477313	0.0477313	0.0477313	0.0477313
rg	4.77313e-10	11.0544	4.77313e-10	11.0544



P7-31 No solution will be given

P7-32

Mole balances in a CSTR

$$DC_{S0} - DC_S + r_S = 0$$

$$-DC_P - r_P = 0$$

$$C_{S0} - C_S = \frac{r_P}{D}$$

$$C_P = \frac{r_P}{D}$$

the rate law as given is:

$$r_P = -r_S$$

$$r_P = \frac{V_{max} C_S}{K_S + C_S} \left(1 - \frac{C_P}{C_P^*} \right)$$

Plugging those into POLYMATH and using different values of D and C_P , come up with the following:

Using a volume of 200 dm³ and a cell concentration of 50, get the best production of the L-malic acid.

Equations:

$$f(cs) = cs - cs0 + rp/D$$

$$f(cp) = cp - rp/D$$

$$cs0 = 2$$

$$D = 50$$

$$cc = 50$$

$$vmax = 76$$

$$km = .048$$

$$cpstar = 1.69$$

$$rp = vmax * cs / (km + cs) * (1 - cp/cpstar) * cc$$

Initial Value

4

2

Variable	<u>Solution</u>	
	Value	f()
cs	0.351657	3.222e-15
cd	1.54834	-3.277e-15
cs0	2	
D	50	
cc	50	
vmax	76	
km	0.048	
cpstar	1.69	
rp	82.4171	

CDP7-A

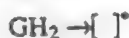
Given the reaction



- 1) $-\text{r}_{\text{GH}_2} = \text{F}(\text{C}_{\text{GH}}, \text{C}_{\text{GH}_2})$
- 2) $-\text{r}_{\text{GH}_2}$ decreases as C_{GH} increases
- 3) With no GH , $-\text{r}_{\text{GH}_2} \propto \text{C}_{\text{GH}_2}$
- 4) With high C_{GH} and low C_{GH_2} , $-\text{r}_{\text{GH}_2} \propto \text{C}_{\text{GH}_2}^2$

A rate law suggested from the observations above is: $-\text{r}_{\text{GH}_2} = \frac{k_1 \text{C}_{\text{GH}_2}^2}{\text{C}_{\text{GH}_2} + k_2 \text{C}_{\text{GH}}}$

This equation suggests the overall reaction mechanism steps:



Therefore, a mechanism based on the information above is proposed:



$$-r_1 = k_1 \text{C}_{\text{GH}_2} - k_{-1} \text{C}_{\text{GH}} \text{C}_{\text{H}^*}$$



$$-r_2 = k_2 \text{C}_{\text{GH}_2} \text{C}_{\text{H}^*}$$

$$-\text{r}_{\text{GH}_2} = k_1 \text{C}_{\text{GH}_2} - k_{-1} \text{C}_{\text{GH}} \text{C}_{\text{H}^*} + k_2 \text{C}_{\text{H}^*} \text{C}_{\text{GH}_2}$$

$$\text{C}_{\text{H}^*} \approx 0 = -k_1 \text{C}_{\text{GH}_2} + k_{-1} \text{C}_{\text{GH}} \text{C}_{\text{H}^*} + k_2 \text{C}_{\text{H}^*} \text{C}_{\text{GH}_2}$$

$$\therefore \text{C}_{\text{H}^*} = \frac{k_1 \text{C}_{\text{GH}_2}}{k_{-1} \text{C}_{\text{GH}} + k_2 \text{C}_{\text{GH}_2}}$$

$$-\text{r}_{\text{GH}_2} = k_1 \text{C}_{\text{GH}_2} + [k_2 \text{C}_{\text{GH}_2} - k_{-1} \text{C}_{\text{GH}}] \left[\frac{k_1 \text{C}_{\text{GH}_2}}{k_{-1} \text{C}_{\text{GH}} + k_2 \text{C}_{\text{GH}_2}} \right]$$

$$= \left[\frac{k_1 k_{-1} \text{C}_{\text{GH}} \text{C}_{\text{GH}_2} + k_1 k_2 \text{C}_{\text{GH}_2}^2 + k_1 k_2 \text{C}_{\text{GH}_2}^2 - k_{-1} \text{C}_{\text{GH}} k_1 \text{C}_{\text{GH}_2}}{k_{-1} \text{C}_{\text{GH}} + k_2 \text{C}_{\text{GH}_2}} \right]$$

$$-\text{r}_{\text{GH}_2} = \left[\frac{2k_1 k_2 \text{C}_{\text{GH}_2}^2}{k_{-1} \text{C}_{\text{GH}} + k_2 \text{C}_{\text{GH}_2}} \right]$$

CDP7-B

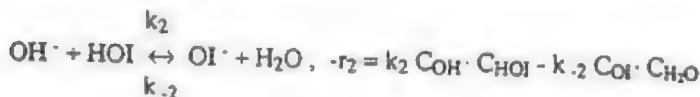
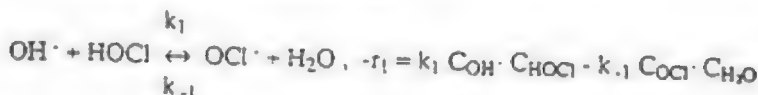
Given the following reaction scheme:



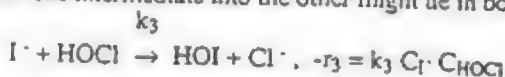
with the following rate law: $r_{OI^-} = \frac{k_{Cl^-} \cdot C_{OCl^-}}{C_{OH^-}}$

Active intermediates assumed to be HOCl and HOI.

From table I, the first rule of thumb suggests:



The third rule of thumb suggests that the reverse reactions occur. A chain propagation step, involving the conversion of one intermediate into the other might tie in both the reactions above.



This step makes the overall reaction sequence $I^- + OCl^- \rightarrow OI^- + Cl^-$ possible:

$$-r_{OI^-} = r_2 = k_{-2} C_{OI^-} \cdot C_{H_2O} - k_2 C_{OH^-} \cdot C_{HOI}$$

$$-r_{HOI} = -r_2 + r_3 = k_2 C_{OH^-} \cdot C_{HOI} - k_{-2} C_{OI^-} \cdot C_{H_2O} - k_3 C_{I^-} \cdot C_{HOCl} = 0$$

$$k_3 C_{I^-} \cdot C_{HOCl} = k_2 C_{OH^-} \cdot C_{HOI} - k_{-2} C_{OI^-} \cdot C_{H_2O} = -r_{OI^-}$$

$$-r_{HOCl} = -r_1 - r_3 = k_1 C_{OH^-} \cdot C_{HOCl} - k_{-1} C_{OCl^-} \cdot C_{H_2O} + k_3 C_{I^-} \cdot C_{HOCl} = 0$$

$$\text{or } [k_1 C_{OH^-} + k_3 C_{I^-}] C_{HOCl} = k_{-1} C_{OCl^-} \cdot C_{H_2O}; \text{ i.e., } C_{HOCl} = \frac{k_{-1} C_{OCl^-} \cdot C_{H_2O}}{k_1 C_{OH^-} + k_3 C_{I^-}}$$

$$\text{Then: } -r_{OI^-} = \frac{k_{-1} k_3 C_{I^-} \cdot C_{OCl^-} \cdot C_{H_2O}}{k_1 C_{OH^-} + k_3 C_{I^-}} \text{ is close; with } k_1 \gg k_3$$

$$-r_{OI^-} = \frac{K C_{I^-} \cdot C_{OCl^-}}{C_{OH^-}} \text{ where } K = \frac{k_{-1} k_3}{k_1}$$

An alternative approach assumes that reaction 1 quickly attains equilibrium, then:

$$C_{HOCl} = \frac{k_{-1} C_{OCl^-} \cdot C_{H_2O}}{k_1 C_{OH^-}}$$

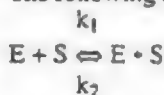
$$\text{Then } -r_{OI^-} = k_3 C_{I^-} \cdot C_{HOCl} = \left[\frac{k_3 k_{-1} C_{H_2O}}{k_1} \right] \frac{C_{I^-} \cdot C_{OCl^-}}{C_{OH^-}}$$

These two approaches are basically equivalent

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CDP7-C

The following enzymatic reaction



(a) Non-inhibition:

$$r_p = k_F [E \cdot S]$$

$$r_{E \cdot S} = k_1 [E][S] - k_2 [E \cdot S] - k_F [E \cdot S]$$

$r_{E \cdot S} = 0$ by the pseudo steady-state hypothesis

$$\therefore [E \cdot S] = \frac{k_1 [E][S]}{k_2 + k_F} \quad \text{with } [E_t] = [E] + [E \cdot S]$$

$$[E_t] = [E] + \frac{k_1 [E][S]}{k_2 + k_F} = [E] \left[\frac{k_2 + k_F + k_1 [S]}{k_2 + k_F} \right]$$

$$\text{or } [E] = \frac{[E_t] (k_2 + k_F)}{k_2 + k_F + k_1 [S]}$$

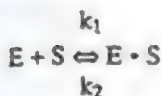
Expression for r_p now becomes:

$$r_p = k_F [E \cdot S] = \frac{k_F k_1 [E][S]}{k_2 + k_F} = \frac{k_1 k_F [S]}{k_2 + k_F} \left[\frac{[E_t] (k_2 + k_F)}{k_2 + k_F + k_1 [S]} \right]$$

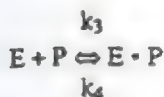
$$r_p = \frac{k_1 k_F [S][E_t]}{k_2 + k_F + k_1 [S]}$$

This expression reduces to equation 7-44 of the text.

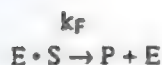
(b) For competitive product inhibition, reaction scheme is of the form:



$$r_1 = k_1 [E][S] - k_2 [E \cdot S]$$



$$r_2 = k_3 [E][P] - k_4 [E \cdot P]$$



$$r_3 = k_F [E \cdot S]$$

$$r_A = r_3 = k_F [E \cdot S]$$

7-60

$$r_{E \cdot S} = r_1 - r_3 \equiv 0 = k_1 [E][S] - k_2 [E \cdot S] - k_F [E \cdot S] = 0$$

$$\text{or } [E \cdot S] = \frac{k_1 [E][S]}{k_2 + k_F}$$

$$r_{E \cdot P} = r_3 = 0 = k_3 [E][P] - k_4 [E \cdot P] = 0 \quad \therefore [E \cdot P] = \frac{k_3 [E][P]}{k_4}$$

$$\text{Now } \therefore [E_t] = [E] + [E \cdot S] + [E \cdot P]$$

$$[E_t] = [E] + \frac{k_1 [E][S]}{k_2 + k_F} + \frac{k_3 [E][P]}{k_4} = [E] \left\{ 1 + \frac{k_1 [S]}{k_2 + k_F} + \frac{k_3 [P]}{k_4} \right\}$$

$$[E] = [E_t] \left\{ \frac{k_2 k_4 + k_4 k_F + k_4 k_1 [S] + k_2 k_3 [P] + k_F k_3 [P]}{k_4 (k_2 + k_F)} \right\}$$

$$-r_A = k_F [E \cdot S] = \frac{k_1 k_F [E][S]}{k_2 + k_F}$$

$$= \frac{k_1 k_F [S]}{k_2 + k_F} \left\{ \frac{k_4 (k_2 + k_F)}{k_2 k_4 + k_4 k_F + k_4 k_1 [S] + k_2 k_3 [P] + k_F k_3 [P]} \right\} [E_t]$$

Rearranging $(-r_A)$:

$$-r_A = \frac{k_F [E_t][S]}{[S] + \frac{k_2 + k_F}{k_1} \left\{ 1 + \frac{k_3 [P]}{k_4} \right\}}$$

This expression is similar to Eq 7-67 with K_m replaced by $\frac{k_2 + k_F}{k_1}$, k by k_F , and $[I]$ with $[P]$.

(c) (a) Product inhibition, noncompetitive reaction scheme is:



Assume reaction (5) controls, then



$$r_1 / k_1 \equiv 0, \quad r_2 / k_2 \equiv 0, \quad r_3 / k_3 \equiv 0, \quad \frac{r_4}{k_4} \equiv 0$$



$$\text{or } [E \cdot S] = K_1 [E][S]$$



$$-r_A = k_F [E \cdot S]$$

$$[E_t] = [E] + [E \cdot S] + [E \cdot P] + [E \cdot S \cdot P]$$

$$[E_t] = [E] + K_1 [E] [S] + K_1 [E] [P] + K_1 K_3 [E] [S] [P]$$

$$\text{or } [E] = \frac{[E_t]}{1 + K_1 [S] + K_2 [P] + K_3 [S] [P]} \quad \text{Then } -r_A = k_F [E \cdot S] = k_F K_1 [E] [S]$$

$$\text{Now } -r_A = \frac{k_F K_1 [S] [E_t]}{1 + K_1 [S] + K_2 [P] + K_1 K_3 [S] [P]}$$

This equation is similar to equation 7-86 of the text, with I replaced by P and k_p by k_F .

(b) Product inhibition of the uncompetitive type: Reaction scheme is of the form:



Rate of formation of P: $r_p = r_1 - r_2$; by pseudo steady-state hypothesis:

$$r_{E \cdot S \cdot P} = r_2 \equiv 0 = k_3 [P] [E \cdot S] - k_4 [E \cdot S \cdot P] \Rightarrow [E \cdot S \cdot P] = \frac{k_3}{k_4} [P] [E \cdot S]$$

$$r_{E \cdot S} = r_1 - r_2 - r_3 = r_1 - r_3 \equiv 0 = k_1 [E] [S] - k_2 [E \cdot S] - k_F [E \cdot S] \Rightarrow [E \cdot S] = \frac{k_1 [E] [S]}{k_2 + k_F}$$

$$[E \cdot S \cdot P] = \frac{k_1 k_3 [E] [S] [P]}{k_4 (k_2 + k_F)}; E_t = [E] + [E \cdot S] + [E \cdot S \cdot P]$$

$$E_t = [E] + \frac{k_1 [E][S]}{k_2 + k_F} + \frac{k_1 k_3 [E][S][P]}{k_4 (k_2 + k_F)} = [E] \left(\frac{k_2 + k_F + k_1 [S] + \frac{k_1 k_3}{k_4} [S][P]}{k_2 + k_F} \right)$$

$$r_p = r_s = k_F [E \cdot S]$$

$$r_p = \frac{k_F [S] [E_t]}{\frac{k_2}{k_1} + \frac{k_F}{k_1} + [S] + \frac{k_3}{k_4} [S][P]}$$

This equation is similar to Eq7-72 of the text, with k_1 replaced by k_F , V_{max} by $k_F [E]$, $[P]$ by $[I]$, K_m by $\frac{k_2 + k_F}{k_1}$ and K_I by $\frac{k_4}{k_3}$.

CDP7-D

- a) Find the equilibrium conversion.

$$K_G = \frac{[E][G]}{[E \cdot S]} \quad K_F = \frac{[E][F]}{[E \cdot S]}$$

$$[E][G]K_F = [E][F]K_G$$

$$[G] = [G]_0 (1 - X_e)$$

$$[F] = [G]_0 X_e$$

$$\frac{X_e}{1 - X_e} = \frac{K_F}{K_G}$$

$$X_e = 0.5$$

- b) 60% of $X_e = .3$

Design equation:

$$\frac{dX}{dt} = \frac{-r_G}{C_{G0}}$$

Rate law:

$$-r_G = \frac{E_t ((k_3 C_G)/K_G - (k_2 C_F)/K_F)}{1 + (C_G/K_G) + (C_F/K_F)}$$

Stoichiometry:

$$C_G = C_{G0} (1 - X)$$

$$C_F = C_{G0} X$$

$$E = 15$$

Combining and using POLYMATH the answer is 4.4 h.

CDP7-D cont'd

Equations:

$$d(\tau)/d(x) = G_0 / -rg$$

$$G_0 = 2$$

$$v = 1$$

$$E = 15$$

$$k_3 = .015$$

$$K_g = .15$$

$$k_2 = .015$$

$$K_f = .15$$

$$c_g = G_0(1-x)$$

$$c_f = G_0 x$$

$$N_{g0} = G_0 / v$$

$$r_f = E \cdot \{ (k_2 \cdot c_g) / K_g - (k_3 \cdot c_f) / K_f \} / (1 + c_g / K_g + c_f / K_f)$$

$$rg = -r_f$$

$$x_0 = 0, \quad x_f = 0.3$$

Initial value

0

7-D

Variable	Initial value	Maximum value	Minimum value	Final value
x	0	0.3	0	0.3
τ	0	4.37783	0	4.37783
G ₀	2	2	2	2
v	1	1	1	1
E	15	15	15	15
k ₃	0.015	0.015	0.015	0.015
K _g	0.15	0.15	0.15	0.15
k ₂	0.015	0.015	0.015	0.015
K _f	0.15	0.15	0.15	0.15
c _g	2	2	1.4	1.4
c _f	0	0.6	0	0.6
N _{g0}	2	2	2	2
r _f	0.209302	0.209302	0.0837209	0.0837209
rg	-0.209302	-0.0837209	-0.209302	-0.0837209

c) Use same equations except $E = E_0 e^{-0.2x}$.

Using POLYMATH the answer is 10.4 h.

Equations:

$$d(\tau)/d(x) = G_0 / -rg$$

$$G_0 = 2$$

$$v = 1$$

$$E = 15 \cdot \exp(-0.2 \cdot x)$$

$$k_3 = .015$$

$$K_g = .15$$

$$k_2 = .015$$

$$K_f = .15$$

$$c_g = G_0(1-x)$$

$$c_f = G_0 x$$

$$N_{g0} = G_0 / v$$

$$r_f = E \cdot \{ (k_2 \cdot c_g) / K_g - (k_3 \cdot c_f) / K_f \} / (1 + c_g / K_g + c_f / K_f)$$

$$rg = -r_f$$

$$x_0 = 0, \quad x_f = 0.3$$

Initial value

0

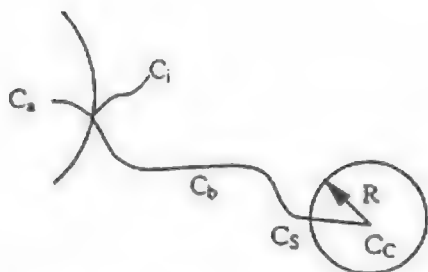
7-64

CDP7-D cont'd

Variable	Initial value	Maximum value	Minimum value	Final value
x	0	0.3	0	0.3
s	0	10.4199	0	10.4199
Go	2	2	2	2
v	1	1	1	1
z	15	15	1.8665	1.8665
k3	0.015	0.015	0.015	0.015
xg	0.15	0.15	0.15	0.15
k2	0.015	0.015	0.015	0.015
xf	0.15	0.15	0.15	0.15
cg	2	2	1.4	1.4
cf	0	0.6	0	0.6
Ng0	2	2	2	2
rf	0.209302	0.209302	0.0104177	0.0104177
rg	-0.209302	-0.0104177	-0.209302	-0.0104177

A conversion of 0.3 will be achieved quicker if a bigger K_f is used. A larger K_G will have the opposite effect and the conversion will be achieved at a slower rate. The value of k_2 has the same effect as K_f and k_3 has a similar effect to K_G .

CDP7-E No solution will be given



(a) Assumptions:

- Transfer rate from bubble bulk to fluid interface is not rate limiting, i.e., C_i is the equilibrium oxygen concentration.
- System is at pseudo steady-state with regard to the particle size, i.e., particle growth is slow compared to oxygen transfer.
- Rate of oxygen consumption is directly proportional to the cell growth rate:

$$r_{O_2} = \frac{1}{y_{O_2}} r_C \quad \text{where } y_{O_2} = \text{yield of cells on oxygen} \left(\frac{\text{g cells}}{\text{mmole } O_2} \right)$$

This implies that any oxygen utilization required to maintain the cells is negligible, and there is no significant metabolic product being synthesized.

$$\begin{aligned} \text{Oxygen balance:} \quad R_{O_2} &= k_1 a_b (C_i - C_b) \\ &= k_1 a_b C_c (C_b - C_s) \\ &= \frac{\eta}{y_{O_2}} k C_s C_c \end{aligned}$$

where:

- $k_1 a_b$ = overall mass transfer resistance from the bubble to the bulk.
- a_c = surface area per gram of cells
- k = mass transfer of cells on O_2
- y_{O_2} = yield of cells on O_2

Rearrange O_2 balances:

$$\frac{R_{O_2}}{k_1 a_b} = C_i - C_b \quad (1)$$

$$\frac{R_{O_2}}{k_c a_c C_c} = C_b - C_s \quad (2)$$

$$\frac{y_{O_2} R_{O_2}}{\eta k C_c} = C_s \quad (3)$$

Add equations 1, 2 and 3

$$\frac{C_i}{R_{O_2}} = \frac{1}{k_1 a_b} + \frac{1}{C_c} \left(\frac{1}{k_c a_c} + \frac{y_{O_2}}{\eta k} \right) \quad (4)$$

(1) When oxygen consumption by the cells is slow, the process is reaction rate limited.

$$\text{Thus } \eta \rightarrow 1 \quad \text{and:} \quad \frac{C_i}{R_{O_2}} = \frac{1}{k_1 a_b} + \frac{y_{O_2}}{C_c k}$$

- (2) When oxygen consumption is much faster than mass transfer, the mass transfer becomes the limiting factor.
$$\frac{C_i}{R_{O_2}} = \frac{1}{k_1 a_b} + \frac{1}{k_c a_c C_c}$$

(b) To increase the growth rate, you could:

- Increase $k_1 a_b$ by increasing fermentor agitation.
- Increase the concentration of cells (since this is an autocatalytic reaction)
- Increase clump surface area and the effectiveness factor by decreasing the particle size (also by increasing fermentor agitation).

(c) $R_C = y_{O_2} R_{O_2}$ From equation (4), have:

$$\begin{aligned} \frac{R_C}{C_i} &= y_{O_2} \left[\frac{1}{k_1 a_b} + \frac{1}{C_c} \left(\frac{1}{k_c a_c} + \frac{y_{O_2}}{\eta k} \right) \right]^{-1} \\ &= y_{O_2} C_c \left[\frac{C_c}{k_1 a_b} + \frac{1}{k_c a_c} + \frac{y_{O_2}}{\eta k} \right]^{-1} \end{aligned}$$

$$\int_{C_0}^{C_c} \frac{1}{y_{O_2} C_c C_i} \left[\frac{C_c}{k_1 a_b} + \frac{1}{k_c a_c} + \frac{y_{O_2}}{\eta k} \right] dC_c = \int_0^t dt$$

$$\frac{C_c - C_{C0}}{k_1 a_b} + \left(\frac{1}{k_c a_c} + \frac{y_{O_2}}{\eta k} \right) \ln \frac{C_c}{C_{C0}} = y_{O_2} C_i t$$

(d) Assumptions:

- There is a constant number of particles
- Each pellet is roughly spherical and has constant density.

We do not know which resistances are controlling, so we know there are no reaction limitations, but may be either internal or external diffusion limitations.

$$R_C = y_{O_2} C_i \left[\frac{1}{k_1 a_b} + \frac{1}{C_c} \left(\frac{1}{k_c a_c} + \frac{y_{O_2}}{\eta k} \right) \right]^{-1}$$

As particle growth increases, k_c , a_c and η will change as functions of the particle diameter. Thus need to find particle diameter as a function of C_c

$$C_c = n \rho_c V_c$$

where n = number concentration of particles (1/l)

$$V_c = \frac{\pi}{6} d_p^3$$

ρ_c = the density of the particles (g/l)

$$d_p^3 = \frac{6 C_c}{\pi n \rho_c}$$

V_c = particle volume (l)

Internal diffusional resistance can be modeled as:

$$\frac{1}{\eta k} = \alpha_1 d_p$$

External diffusional resistance with or without shear is:

$$\frac{1}{k_c a_c} = \alpha_2 d_p^b \quad 1.5 \leq b \leq 2$$

$$R_C = y_{O_2} C_i \left[\frac{1}{k_1 a_b} + \frac{1}{C_c} \left(\alpha_1 d_p + y_{O_2} \alpha_2 d_p^b \right) \right]^{-1}$$

CDP7-F (cont'd)

$$R_C = y_{O_2} C_i \left[\frac{1}{k_1 a_b} + \frac{1}{C_C} (\alpha_1 C_C^{1/3} + \alpha_2 C_C^{b/3}) \right]^{-1}$$

where $\alpha_1 = \alpha_1 \frac{6}{\pi n \rho_C}$ and $\alpha_2 = \alpha_2 \frac{6 y_{O_2}}{\pi n \rho_C}$

Dropping the primes and simplifying:

$$R_C = y_{O_2} C_i \left[\frac{1}{k_1 a_b} + \alpha_1 C_C^{-2/3} + \alpha_2 C_C^{b/3-1} \right]^{-1}$$

$$\int_{C_0}^{C_C} \left[\frac{1}{k_1 a_b} + \alpha_1 C_C^{-2/3} + \alpha_2 C_C^{b/3-1} \right] dC_C = \int_0^t y_{O_2} C_i dt$$

$$\frac{C_C - C_{C0}}{k_1 a_b} + 3\alpha_1 (C_C^{1/3} - C_{C0}^{1/3}) + \frac{3\alpha_2}{b} (C_C^{b/3} - C_{C0}^{b/3}) = y_{O_2} C_i t$$

(c) From part (c), we have:

$$\frac{C_C - C_{C0}}{k_1 a_b} + \left(\frac{1}{k_C a_C} + \frac{y_{O_2}}{\eta k} \right) \ln \frac{C_C}{C_{C0}} = y_{O_2} C_i t$$

For a vigorously stirred fermentor, assume that fluid shear is sufficiently high, that transport to the edge of the floc is negligible⁽¹⁾:

$$\frac{1}{k_C a_C} \rightarrow 0$$

The mass transfer resistance from air bubble to bulk liquid depends on the fermentor design, air flow rate, agitation rate and a number of other factors. For a 10 l laboratory scale fermentor, $k_1 a_b$ was found to be $\sim 150 \frac{\text{m Mole}}{\text{l hr atm}}$ during the growth phase of the fermentation.⁽²⁾

Dividing through by Henry's law constant:

$$\begin{aligned} k_1 a_b &= \left(150 \frac{\text{m Mole}}{\text{l hr atm}} \right) \left(0.88 \frac{\text{atm l}}{\text{m Mole}} \right) \left(\frac{1 \text{ hr}}{3600 \text{ s}} \right) \\ &= 3.67 \times 10^{-2} \text{ s}^{-1} \end{aligned}$$

Effectiveness factor: Microbial growth on multiple substrates (here oxygen and glucose) is typically modelled using Monod type kinetics:

$$\mu (\text{hr}^{-1}) = \mu_m \left(\frac{C_N}{K_N + C_N} \right) \left(\frac{C_O}{K_O + C_O} \right)$$

$$R_C = \mu C_C$$

By representing the reaction as first-order with respect to oxygen, we are essentially assuming a low oxygen concentration, relative to the intrinsic rate parameter, K_O :

CDP7-F (cont'd)

$$\frac{C_0}{K_0 + C_0} = \frac{C_0}{K_0}$$

This implies that the consumption of oxygen is diffusion limited inside the pellet, i.e., that the Thiele modulus is large ($\phi > 1$) (See Ref. 1, p.396). In order to check this (and to find the effectiveness factor) we calculate the Thiele modulus. For a first-order reaction in a biological pellet:

$$\phi = \frac{R}{3} \sqrt{\frac{\mu_{\max} \rho_0}{Y_{O_2} K_0 D_0^{\text{eff}}}}$$

maximum specific growth rate $= \mu_{\max} = 0.3 \text{ hr}^{-1} = 8.3 \times 10^{-5} \text{ s}^{-1}$

yield coefficient: $Y_{O_2} = 1.5 \frac{\text{g cell}}{\text{g } O_2}$

Monod constant: $K_0 = 3.2 \times 10^{-7} \frac{\text{g } O_2}{\text{cm}^3}$

Effective diffusivity: $D_0^{\text{eff}} = 1 \times 10^{-5} \frac{\text{cm}^2}{\text{s}}$

Pellet radius: $R = 0.01 \text{ cm}$

Cell density in pellet: $\rho_0 = f_{\text{cell}} \rho_{\text{cell}} = 0.5 \left(\frac{300 \text{ g}}{1} \right) \left(\frac{1}{10^3 \text{ cm}^3} \right)$
 $= 0.15 \text{ g/cm}^3$
 $\phi = 5.4$

For a first-order reaction, the effectiveness factor is:

$$\eta = \frac{3}{\phi^2} (\phi \cosh \phi - 1)$$

$$\eta = 0.45$$

Reaction rate constant:

$$k = \frac{\mu_{\max}}{K_0} = \frac{8.3 \times 10^{-5} \text{ s}^{-1}}{3.2 \times 10^{-4} \frac{\text{g } O_2}{\text{cm}^3}} = 0.26 \frac{1}{\text{g } O_2 \text{ s}}$$

Finally, assume an initial cell concentration of 0.25 g cell/l , the cell concentration equation now becomes:

$$\frac{(C_C - 0.25) \frac{\text{g cell}}{1}}{3.67 \times 10^{-2} \text{ s}^{-1}} + \left[\frac{1.5 \frac{\text{g cell}}{\text{g } O_2}}{(0.45) \left(0.26 \frac{1}{\text{g } O_2 \text{ s}} \right)} \right] \ln 4C_C = \left(1.5 \frac{\text{g cell}}{\text{g } O_2} \right) \left(7.7 \times 10^{-3} \frac{\text{g } O_2}{1} \right) t$$

$$27.25 (C_C - 0.25) + 12.8 \ln 4C_C = 0.012 t$$

Clearly, mass transfer from the gas to the liquid phase and internal diffusion play important roles in determining the cell growth rate.

CDP7-F (cont'd)

Cell mas vs time. Start at 0.25 g/l

t (hr)	C _c (g/l)	t (hr)	C _c (g/l)
0	0.25	8	11.15
1	1.13	9	12.67
2	2.37	10	14.21
3	3.74	11	15.74
4	5.17	12	17.28
5	6.64	0.5	0.62
6	8.13	1.5	1.72
7	9.63		

From the graph it can be seen that growth starts out exponentially and becomes linear as the fermentation becomes limited by gas-liquid mass transfer.

Sensitivity analysis:

The gas-liquid mass transfer coefficient is related to the agitation rate to the 0.95 power⁽³⁾: $k_1 a_b \propto N^{0.95}$

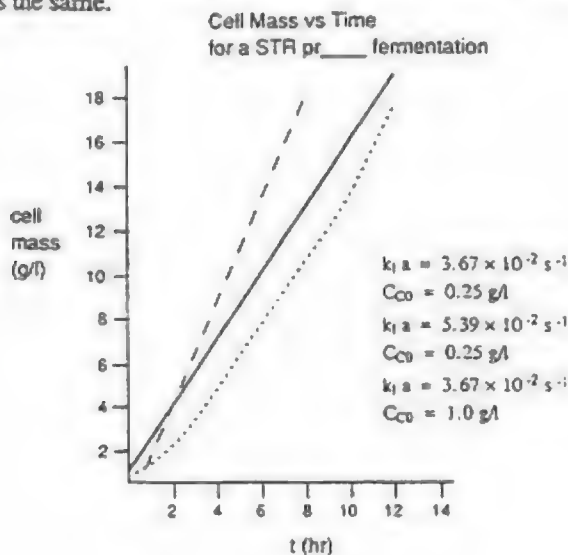
What is the effect of increasing the agitation by 50%?

$$\begin{aligned}
 k_1 a_2 &= k_1 a_1 (1.5^{0.95}) \\
 &= (3.67 \times 10^{-2}) \text{ s}^{-1} (1.5^{0.95}) \\
 &= (5.39 \times 10^{-2}) \text{ s}^{-1} \quad (\text{see graph})
 \end{aligned}$$

Since cell growth has an exponential portion, another way to increase the growth rate would be to increase the innocuous size, C_{co}. What happens when C_{co} is quadrupled?

$$C_{co} = 1.0 \text{ g/l} \quad (\text{see graph})$$

From the results shown in the graph, a relatively small increase in the agitation rate leads to a significant increase in the cell growth rate, while an increase in inoculum size means that the fermentation reaches a gas-liquid transfer-limited state more quickly, but the growth rate remains the same.



References:

- (1) James E. Bailey and David F. Ollis, Biochemical Engineering Fundamentals, (NY: McGraw-Hill, 1977), Chapters 7 and 8.
- (2) G.F. Payne, PhD Thesis, University of Michigan, (1983).
- (3) D.L.C. Wang, et. al., Fermentation and Enzyme Technology, (NY: John Wiley & Sons, 1979), Chapter 9.

CDP7-G

$$r_B = \mu_{\max} C_B$$

$$r_A = k_a C_A C_B$$

$$-r_{ad} = k_d C_A$$

$$D = F/V$$

Material balance:

$$\frac{dC_B}{dt} = D(C_{Bin} - C_B) + \mu_{\max} C_B - \frac{k_a C_A C_B}{Y_{A/B}}$$

Amoeba Balance

$$\frac{dC_A}{dt} = D(C_{Ain} - C_A) + k_a C_A C_B - k_d C_A$$

steady state $\frac{dC_A}{dt} = \frac{dC_B}{dt} = 0 \quad C_{B_{ex}} = 0 \quad C_{A_{ex}} = 0$

$$DC_B = \mu_{\max} C_B - \frac{k_a C_A C_B}{Y_{A/B}} \quad (1)$$

$$DC_A = k_a C_A C_B - k_d C_A \quad (2)$$

To rectify the contamination problem, have D high enough to wash out amoebas but not bacteria.

wish $C_A = 0$

$$C_B = \frac{D + k_d}{k_a}$$

$$C_A = \frac{D - \mu_{\max}}{k_a} Y_{A/B}$$

CDP7-G (cont'd)

for $C_A = 0$ $D = \mu_{\max}$ No amoebas after reaching steady state.

$$C_B = \frac{\mu_{\max} + k_d}{k_s} = \frac{0.5 + 0.01}{0.5} = 0.22 \frac{g}{dm^3} \text{ final bacterial concentration when } C_A = 0$$

b) $C_{Bw} = 0$ $C_{Aw} = 0$ then Bacteria and Amoeba Balance becomes

$$\begin{aligned} \frac{dC_B}{dt} &= (\mu_{\max} - D) C_B - \left(\frac{k_s C_A C_B}{Y_{A/B}} \right) \\ \frac{dC_A}{dt} &= k_s C_A C_B - (D + k_d) C_A \end{aligned}$$

$$\begin{aligned} \mu_{\max} &= 0.5 \text{ hr}^{-1} & k_d &= 0.01 \\ D &= 0.04 \text{ hr}^{-1} & Y_{A/B} &= 0.5 \\ k_s &= 0.5 & C_{A0} &= 0.1 \\ & & C_{B0} &= 1.0 \end{aligned} \quad \left. \vphantom{\begin{aligned} \mu_{\max} &= 0.5 \text{ hr}^{-1} \\ D &= 0.04 \text{ hr}^{-1} \\ k_s &= 0.5 \\ C_{A0} &= 0.1 \\ C_{B0} &= 1.0 \end{aligned}} \right\} \text{ at } t = 0$$

7-G

Equations:

$$d(cb)/d(\tau) = (1.5 - d) \cdot cb - 0.5 \cdot ca \cdot cb$$

$$d(ca)/d(\tau) = 0.5 \cdot ca \cdot cb - (d + 0.01) \cdot ca$$

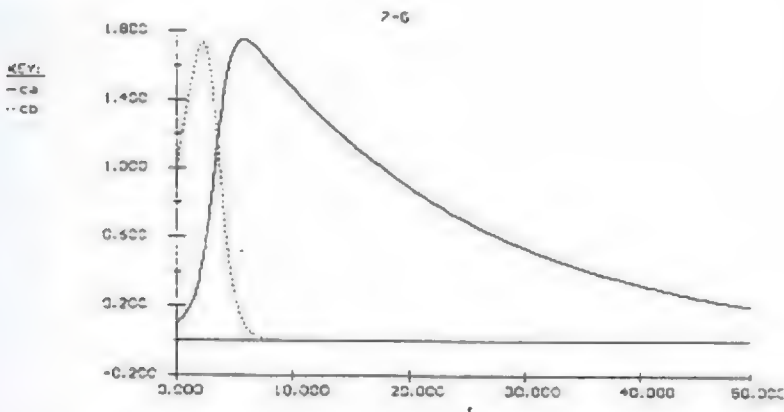
$$d = 0.04$$

$$\tau_0 = 0, \quad \tau_f = 50$$

Initial value

1

0.1



CDP7-H No solution will be given

7-72

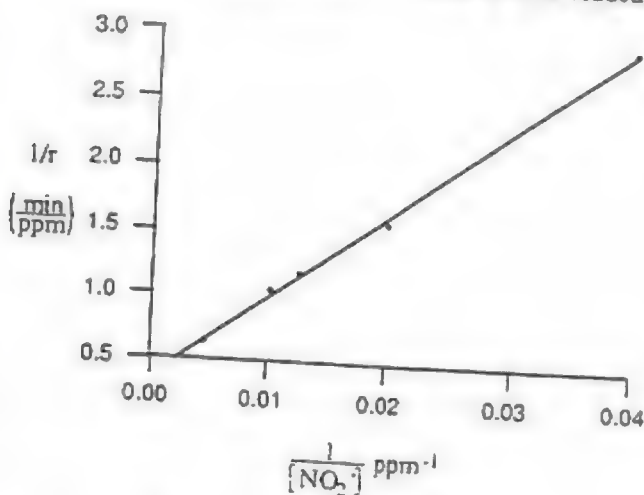
CDP7-I

Since the denitrification follows Michaelis-Menton kinetics, first determine V_{max} and K_m from Lineweaver Burk plot.

Initial $[NO_2^-]$ (ppm)	$\frac{1}{[NO_2^-]}$	Time for 50.6° reduction. (min)	Rate of reaction r , (ppm/min)	$1/r$
25	.04	35	.357	2.800
50	.02	38	.658	1.520
75	.013	44	.852	1.173
100	.010	50	1.000	1.000
200 (given)	.005	66 (given)	1.515	0.660

where the rate of reaction is found by the ratio:

$$\frac{\text{initial } [NO_2^-] / 2}{\text{time for 50\% reduction}}$$



Lineweaver Burk: $\frac{1}{r} = \left(\frac{K_m}{V_{max}} \right) \frac{1}{S} + \frac{1}{V_{max}}$ where $S = [NO_2^-]$

From the plot, $V_{max} = \frac{1}{\text{intercept}} = 2.73 \frac{\text{ppm}}{\text{min}}$

$\therefore K_m = 165 \text{ ppm}$

Next, need conversion as a function of time.

Design equation: $N_{S0} \frac{dX}{dt} = -r_S V$

CDP7-I (cont'd)

Rate Law: $-r_S = \frac{V_{\max} S}{K_m + S}$

Stoichiometry: $S = S_0 (1 - X)$

Combining: $S_0 \frac{dX}{dt} = V_{\max} S_0 \left[\frac{1 - X}{K_m + S_0 (1 - X)} \right]$

$$\int_0^X \frac{K_m + S_0 (1 - X)}{(1 - X)} dX = V_{\max} \int_0^t dt$$

$$\therefore K_m \ln \left(\frac{1}{1 - X} \right) + S_0 X = V_{\max} t$$

Finally, $V_{\max} t = S_0 X - K_m \ln (1 - X)$

Know V_{\max} , K_m , $t = 68 \text{ hrs} = 4080 \text{ min}$

$$S_0 = 0.25 \left(\frac{\text{mol}}{\text{l}} \right) \left(46 \frac{\text{g}}{\text{mol}} \right) \left(\frac{1000 \text{ mg}}{\text{g}} \right) \left(\frac{1 \text{ ppm}}{\text{mg/l}} \right) = 11,500 \text{ ppm}$$

Iteration to find the conversion obtained after 68 hrs gives: $X = 0.930$

The $[\text{NO}_2^-]$ level is: $(1 - 0.930) (11,500 \text{ ppm}) = 805 \text{ ppm}$

Since t , K_m , and S_0 are fixed by the system, the change must be made in V_{\max} .

Desired conversion: $X = 1 - \frac{500}{11,500} = .9565$

$$\therefore \text{Desired } V_{\max} = \frac{11,500 (.9565) - 165 \ln (1 - .9565)}{4080} = 2.823 \frac{\text{ppm}}{\text{min}}$$

Since $V_{\max} \propto [E]$, increasing the concentration of whole cells in the emulsion will increase

$$V_{\max} : \left(\frac{2.823}{273} \right) 50 \frac{\text{mg cells}}{\text{ml emulsion}} = 51.7 \frac{\text{mg cells}}{\text{ml emulsion}}$$

Therefore, increasing the cell loading to $52 \frac{\text{mg cells}}{\text{ml emulsion}}$ would result in a level of $[\text{NO}_2^-] < 500 \text{ ppm}$ after 68 hours.

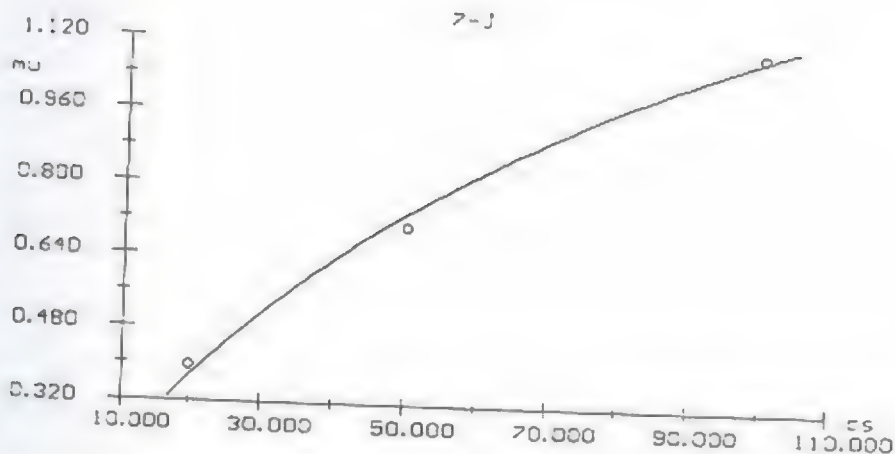
CDP7-I

a) Find the μ value by dividing r_g by C_c .

μ	C_s
1.1	100
.71	50
.4	20

Using POLYMATH, find the values for μ_{\max} and K_s .

They are: $\mu_{\max} = 2.1$
 $K_s = 92.2$



Model: $\mu = \mu_{\max} \times C_s / (K_s + C_s)$

$\mu_{\max} = 2.09665$

$K_s = 92.2253$

2 positive residuals, 1 negative residuals. Sum of squares = 0.00151407

b) Using the equation :

$$V = \frac{m_p}{Y_{p/c} r_g}$$

$$Y_{p/c} = \frac{Y_{p/s}}{Y_{c/s}} = .11$$

$$C_s = C_{s0} - C_c Y_{c/s} = 77.8$$

$$r_g = \frac{\mu_{\max} C_s C_c}{K_s + C_s} = 19$$

$$V = 9.57 \text{ dm}^3$$

Chapter 8

- P8-1. An open-ended problem that requires students to create and original problem and solution.
- P8-2. "What if. . ." problem. Many good extensions of the Living Example problems. Choose one or two parts (c) through (k) and alternate parts assigned form year to year. Part (d) is the easiest.
- P8-3. Actual case history. This problem is continued in Chapter 9, P9-3. The point of this problem is to calculate the conditions at the time the CSTR feed was shut off. Fairly straight forward. The students have to use the enthalpy balance that includes phase change.
- P8-4. Very good California problem. It takes some time for the students to realize that there is essentially complete conversion ($X=1$) and that work is done on the system.
- P8-5. This problem concerns a liquid phase reaction carried out adiabatically. Parts (a) through (d) are straight forward and reinforce the principle of non-isothermal reactor design. Part (e) asks for a sensitivity analysis (i.e. parameter variation).
- P8-6. This problems concerns an adiabatic gas phase reaction. The students sometimes forget that the gas phase reaction the concentration is a function of temperature. Overall this is a very straight forward problem.
- P8-7. This problem extends P8-6 to include pressure drop. Very straight forward using POLYMATH. However, one may run into trouble during the integration if α is to large and have to use the POLYMATH stiff algorithm.
- P8-8. This problem encompasses all the facets of non-isothermal PBR and CSTRs with heat exchange. Fairly straight forward with POLYMATH and reinforces the concepts. This problem can be alternated form year to year with P8-9, P8-12, and P8-15.
- P8-9. Same comments as for P8-8 except it does not have any CSTR calculations. Alternate with P8-8, P8-12, and P8-15.
- P8-10. This problem shows the competing effects of adding an inert to an endothermic reaction. The students are asked to find the concentration (flow rate) of inert that maximizes the conversion. A straight forward problem. That can be alternated with P8-23.
- P8-11. This problem requires the student to apply the energy balance to a membrane reactor. The student will have to derive the necessary relationships from first principles because there are not formulas given for membrane reactors with heat effects in the book.

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- P8-12. Same comments as for P8-8 except there are no CSTR calculations. Alternate with P8-8, P8-9, and P8-15.
- P8-13. Straight forward problem involving reactor staging.
- P8-14. No calculations are required in this somewhat complex problem on reactor staging.
- P8-15. Same comments as for P8-8, however, even though this reaction is reversible, the problem is fairly straight forward.
- P8-16. This problem is a very slightly more difficult problem on reactor staging than P8-13, yet is reasonably straight forward.
- P8-17. This is a straight forward problem on multiple steady states. Alternate to P8-20, P8-21, and P8-22.
- P8-18. This problem is usually assigned at the graduate level.
- P8-19. Problem involving calculating the conditions for the reaction to RUNAWAY.
- P8-20. Same comments as P8-17. Alternate to P8-17, P8-21, and P8-22.
- P8-21. Same comments as P8-17. Alternate to P8-17, P8-20, and P8-22.
- P8-22. This problem is the most often problem assigned of the multiple steady state problems.
- P8-23. Find the optimum feed rate of inerts for Living Example 8-7. Similar to P8-10.
- P8-24. Derivation of energy balance to include radial temperature gradients. Assigned only at the graduate level.
- Problems P8-25 through P8-27 concern using Living Example Problem E8-10 to study different effects and conditions for the SO_2 oxidation.
- Problems P8-28 through P8-32 involve multiple reactions with heat effects. In my mind these problems are one of the pinnacles, if not *the* pinnacle of an undergraduate course in chemical reaction engineering.
- P8-28. This problem concerns series reaction with heat effects in a CSTR. The instruction could extend the problem statement in the text to ask the students to carry out a parameter sensitivity. E.g. increase/decrease/ E_1 and E_2 . This problem could be alternated with P8-31, which involves parallel reactions.

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- P8-29. Encompasses all the aspects of multiple reactions with heat effect. Fairly straight forward problem with POLYMATH.
- P8-30. This problem on the production of styrene is almost always assigned. It encompasses all the facets of multiple reactions with heat effects. The students will be able to find an optimum inlet temperature and an optimum inert flow rate. Double or triple credit is often assigned for this problem.
- P8-31. Parallel reactions with heat effects in a CSTR. Quite straight forward using the POLYMATH non-linear equation solver.
- P8-32. <Prof. Fogler: Anything going here?>
- CDP8-A Very straight forward.
- CDP8-B Assigned at graduate level.
- CDP8-C Assigned at graduate level.
- CDP8-D Assigned at graduate level.
- CDP8-E Continuation of problems P8-26 and P8-27.
- CDP8-F Continuation of problems P8-26 and P8-27.
- CDP8-G Continuation of problems P8-26 and P8-27.
- CDP8-H Straight forward problem of parallel reactions H with heat effects.
- CDP8-I Alternative to problems P8-20, P8-21, P8-22, CDP8-?, and CDP8-N.
- CDP8-J Straight forward problem of series reactions with heat effects.
- CDP8-K No so straight forward of multiple reaction with heat effects.
- CDP8-L More complicated version of Problems P8-20, P8-21, and P8-22.
- CDP8-M Alternative to P8-20, P8-21, and P8-22.
- CDP8-N More complicated version of P8-20, P8-21, and P8-22.
- CDP8-O Straight forward problem of multiple reactions O with heat effects.
- CDP8-P Straight forward alternative to P8-6.

	<u>Assigned</u>	<u>Alternates</u>	<u>Difficulty</u>	<u>Time</u>	<u>Solution Given</u>
P8-1				-	No
● P8-2				120	No
● P8-3			FSF	45	Yes
● P8-4			FSF	30	Yes
● P8-5	AA	6,J,N	SF	75	Yes
P8-6	AA	5,J,N	SF	50	Yes
P8-7	O		SF	30	Yes
● P8-8	AA	9,12	SF	75	Yes
P8-9	AA	8,12	SF	60	Yes
● P8-10		23	SF	60	Yes
P8-11	G		MD	75	Yes
P8-12	AA	8,9	FSF	60	Yes
● P8-13	AA	14,15,16	SF	45	Yes
P8-14	AA	13,15,16	MD	60	Yes
P8-15	AA	13,14,16	FSF	70	Yes
P8-16	AA	13,14,15	SF	45	Yes
P8-17	AA	20,21,22,L	SF	60	Yes
P8-18	G		MD	75	Yes
P8-19	O/G		MD	60	Yes
P8-20	AA	17,21,22,D,L,I	SF	95	Yes
● P8-21	AA	17,20,22,D,L,I	SF	60	Yes
P8-22	AA	17,20,21,D,L,I	FSF	75	Yes
P8-23	O	10	SF	75	Yes
P8-24	G		MD	120	No
● P8-25	G		MD	90	Yes
P8-26	I	27,E,F,G	MD	90	Yes
P8-27	I	26,E,F,G	MD	75	Yes
P8-28	I/G	29,30,31,H	MD	75	Yes
P8-29	AA	28,30,31,H	MD	60	Yes
● P8-30	AA	28,29,31,H	MD	100	Yes
● P8-31	O	28,29,30,H	MD	60	Yes
P8-32				60	Yes
CDP8-A			FSF	75	Yes
CDP8-B	G	C	MD	45	Yes
CDP8-C	G	B	FSF	45	Yes
CDP8-D	I/G	17,20,21,22,L,I	MD	60	Yes
CDP8-E	I/G	26,27,F,G	MD	60	Yes
CDP8-F	I/G	26,27,E,G	MD	60	Yes
CDP8-G	I/G	26,27,E,F	MD	60	Yes
CDP8-H	I	28,29,30,31	MD	45	Yes
CDP8-I	I	17,20,21,22,D,L	FSF	45	Yes
CDP8-J	I	5,8,G	FSF	40	Yes
CDP8-K	G	28,29,30,31,H,I	MD	75	Yes
CDP8-L	G/O	17,20,21,22,D,I	MD	120	Yes
CDP8-M	AA	5,6,J,P	SF	45	Yes
CDP8-N	I	17,20,21,22,D,I,L	MD	60	Yes

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CDP8-O	AA	29,30,31,H,I,J	MD	75	Yes
CDP8-P	O	5,6,J,N	FSF	75	Yes

Assigned

- = Always assigned, AA = Always assign one from the group of alternates, O = Often, I = Infrequently, S = Seldom, G = Graduate level

Alternates

In problems that have a dot in conjunction with AA means that one of the problems, either the problem with a dot or any one of the alternates are always assigned.

Time

Approximate time in minutes it would take a B/B* student to solve the problem.

Difficulty

- SF = Straight forward reinforcement of principles (plug and chug)
- FSF = Fairly straight forward (requires some manipulation of equations or an intermediate calculation).
- IC = Intermediate calculation required
- M = More difficult
- OE = Some parts open-ended.

Note the letter problems are found on the CD-ROM. For example A = CDP1-A.

Summary Table Ch-8

	PFR	PBR	CSTR	Membrane	Staging	MSS	Multiple Reactions
Adiabatic	2(e),5(a), 6(a),10,23		3,5(a,d) 6(b)	11	13,14,16	17,20,21, 22	28,31,32
Non adiabatic	15	7,8,12,26, 27	4,8(c), 15(c),19				28,30
Straight forward	5(a,c),6(a)	8(a),12(a)	5(a,d), 6(b),8(c)		13 16	20 21	30(a,b,c)
Parameter variation	2(c,d,g,h,i) 5(b,e),8(e) 9(b,c), 10(c),12(d))		12(j)				

Chapter 8

P8-1 No solution will be given.

P8-2 No solution will be given.

P8-3

Part I: Find reactor temperature at steady state (prior to shut down).

Let M : mass of NH_4NO_3 in reactor

F_{A0} : lbs/hr NH_4NO_3 fed to reactor

Mass balance: $F_{A0} - F_{A0}(1-X) = -r_A V = kM$

$$X = \frac{k(T)M}{F_{A0}}$$

Energy balance:

$$-F_{A0} \sum \theta_i [H_{i0} - H_i(T)] + F_{A0} X \Delta H_{Rxn}(T) + F_{A0}(1-X) \Delta H_{VA} = 0$$

where $H_i(T)$ is the enthalpy of i at the phase and temperature of the reaction, ΔH_{VA} is the heat of vaporization of A, and $\Delta H_{Rxn}(T)$ is the heat of reaction at the outlet temperature:



The last term $F_{A0}(1-X) \Delta H_{VA}$ accounts for the unreacted NH_4NO_3 , which exits as vapor rather than liquid. Now, we can make some substitutions

$$\theta_B = \frac{0.17}{0.83}, \quad \theta_A = 1; \quad \theta_C = 0$$

Heat capacity of A is given, and the enthalpy change for water $200^\circ\text{F}(l) \rightarrow 500^\circ\text{F}(g)$ is also given. So, after dividing out F_{A0} , we obtain:

$$C_{pA}(T-200) + \theta_B [H_B(500^\circ\text{F}) - H_B(200^\circ\text{F}) + C_{pB}(T-500)] + \Delta H_{Rxn} X + (1-X) \Delta H_{VA} = 0$$

The previous equation assumes that (1) Heat capacities are constant over a reasonable temperature range, and (2) the phase change $\text{NH}_4\text{NO}_3(\text{aqueous}) \rightarrow \text{NH}_4\text{NO}_3(\text{liquid})$ is isenthalpic. In addition, we must account for the effect of the temperature dependence of ΔH_{Rxn}

P8-3 cont'd

$$\Delta H_{Rxn}(T) = \Delta H_{Rxn}(T_r) + (T - T_r) \left[\frac{44}{80} C_{pc} + \frac{36}{80} C_{ps} - C_{pA} \right] = \Delta H_{Rxn}(T_r) + (T - T_r) \Delta C_p$$

Let $\Delta H_w = H_B(500) - H_B(200)$, we have:

$$C_{pA} (T - 200) + \theta_B (\Delta H_w + C_{pB}(T - 500)) + X [\Delta H_{Rxn} + \Delta C_p(T - 500)] + (1 - X) \Delta H_{VA} = 0$$

$$\text{or: } T \{ C_{pA} + \theta_B C_{pB} \} + [-C_{pA}(200) + \theta_B (\Delta H_w - 500 C_{pB})] + X [\Delta H_{Rxn} + \Delta C_p(T - 500)] + (1 - X) \Delta H_{VA} = 0$$

Numerical substitution with.

$$k(560) = 5.03; k(510) = 0.53$$

$$\ln \left(\frac{k_2}{k_1} \right) = - \frac{E_A}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \rightarrow \frac{E_A}{R} = - \ln \left(\frac{k_2}{k_1} \right) \left[\frac{1}{T_2} - \frac{1}{T_1} \right]^{-1}$$

$$\frac{E_A}{R} = - \ln \left(\frac{5.03}{0.53} \right) \left[\frac{1}{560 + 459.67} - \frac{1}{510 + 459.67} \right]^{-1} = 44499$$

$$A_0 = k_1 \exp \left(\frac{E_A}{RT_1} \right) = 4.51424 \times 10^{19}$$

$$C_{pA} = 0.38 \frac{\text{Btu}}{\text{lb} \cdot \text{R}}; C_{pB} = 0.466 \text{ (} P = 1 \text{ atm over } 450 - 500^\circ\text{F Himmelblau)}$$

$$C_{pC} = 0.2521 \frac{\text{Btu}}{\text{lb} \cdot \text{R}} \text{ (Himmelblau, App. E, over } 230 - 265^\circ\text{C)}$$

$$\theta_B = \frac{0.17}{0.83} = 0.205$$

$$\Delta H_w = 1034 \frac{\text{Btu}}{\text{lb}}$$

$$F_{A0} = 257.3 \frac{\text{lb NH}_4\text{NO}_3}{\text{hr}}$$

$$\Delta C_p = \frac{44.02}{80.05} (0.2521) + \frac{36.03}{80.05} (0.466) - 0.38 = -0.0316 \frac{\text{Btu}}{\text{lb} \cdot \text{R}}$$

$$\Delta H_{Rxn} = -336 \frac{\text{Btu}}{\text{lb NH}_4\text{NO}_3}$$

$$\Delta H_{VA} = C_{pA} (410 - T)$$

Substituting all of this into the mass and energy balances:

P8-3 cont'd

$$\text{mass balance: } X = \frac{4.51 \times 10^{19} \exp\left(\frac{-44499.4}{T + 459.67}\right) M}{257.3}$$

Energy balance:

$$0 = 0.48 T + 88.21 + X(-320.20 - 0.03 T) + (1 - X)(155.80 - 0.38 T)$$

Assume $X = 0.96$ and $M = 500$. From mass balance:

$$T = \left[\ln \left[\frac{X F_{A0}}{M_{A0}} \right] / E_A \right]^{-1} - 459.67$$

$$T = 510^\circ\text{F}$$

P8-4 Given: The endothermic liquid phase elementary reaction



Feed	A	B	C
$F_{i0} : \left(\frac{\text{lb mole}}{\text{hr}} \right)$	10	10	0.0
$T_{i0} : (^\circ\text{F})$	80	80	--
$\bar{C}_{P,i} : \left(\frac{\text{Btu}}{\text{lb mole } ^\circ\text{F}} \right)$	51	44	47.5
$\text{MW} : \left(\frac{\text{lb}}{\text{lb mole}} \right)$	128	94	222
$\rho_i : \left(\frac{\text{lb}}{\text{ft}^3} \right)$	63	67.2	65

$$\Delta H_R = 20,000 \text{ Btu/lbmole, } A = \text{constant}$$

Energy balance with work term included is:

$$\frac{Q - W_s}{F_{A0}} - X_A \Delta H_R = \sum \theta_i \bar{C}_{P,i} (T - T_0) ;$$

$$\theta_A = 1, \theta_B = \frac{F_{B0}}{F_{A0}} = \frac{10}{10} = 1, X_{AF} = 1$$

$$Q = UA (T_S - T)$$

Substituting into energy balance,

P8-4 cont'd

$$UA(T_S - T) - \dot{W}_S - F_{A0} \Delta H_R X_{AF} = F_{A0} [C_{pA} + C_{pB}] (T - T_0), \text{ or}$$

$$UA(T_S - T_0) - \dot{W}_S - F_{A0} \Delta H_R = (F_{A0} [C_{pA} + C_{pB}] + UA) (T - T_0), \text{ or}$$

$$T = T_0 + \frac{UA(T_S - T_0) - \dot{W}_S - F_{A0} \Delta H_R}{F_{A0} [C_{pA} + C_{pB}] + UA}$$

$$\dot{W}_S = 25 \text{ hp} \times \frac{2545 \text{ Btu}}{\text{hp} \cdot \text{hr}} = 63,625 \frac{\text{Btu}}{\text{hr}}$$

$$T = 80^\circ\text{F} + \frac{150 \frac{\text{Btu}}{\text{hr ft}^2 \cdot ^\circ\text{F}} \times 10 \text{ ft}^2 (365.9 - T)^\circ\text{F} + 63,625 \frac{\text{Btu}}{\text{hr}} - 10 \frac{\text{lb mol}}{\text{hr}} \times \frac{20,000 \text{ Btu}}{\text{lb mol}}}{10 \frac{\text{lb mol}}{\text{hr}} [51 + 44] \frac{\text{Btu}}{\text{lb mol} \cdot ^\circ\text{F}} + 150 \frac{\text{Btu}}{\text{hr ft}^2 \cdot ^\circ\text{F}} \times 10 \text{ ft}^2}$$

$$T = 199^\circ\text{F}$$

P8-5



$$1) \quad V_{PFR} = F_{A0} \int \frac{dX}{-r_A}, \quad V_{CSTR} = \frac{F_{A0}}{-r_A}$$

$$2) \quad -r_A = k C_A C_B, \quad k = k(300) e^{\frac{E}{R} (\frac{1}{300} - \frac{1}{T})}$$

$$3) \quad \text{Liquid Phase} \quad C_A = C_{A0} (1 - X) \\ C_{A0} = C_{B0} \quad C_B = C_{A0} (1 - X)$$

$$4) \quad \text{Adiabatic}$$

$$T = T_0 + \frac{X(-\Delta H_R(T_0))}{\sum \phi_i \bar{C}_{p,i} + X \Delta \bar{C}_p}$$

$$A) \quad \Delta \bar{C}_p = C_{pC} - C_{pB} - C_{pA} = 30 - 15 - 15 = 0$$

$$\Delta H_R(T) = H_C - H_B - H_A = (-41,000) - (-15,000) - (-20,000)$$

$$B) \quad \Delta H_R(T) = -6,000 \text{ cal/mole A}$$

$$C) \quad \sum \theta_i \bar{C}_{p,i} = C_{pA} + \theta_B C_{pB} = C_{pA} + C_{pB} = 15 + 15 = 30 \text{ cal/mol} \cdot \text{K}$$

$$T = 300 + \frac{6000 X}{30} = 300 + 200 X$$

$$\boxed{T = 300 + 200 X}$$

P8-5 cont'd

5) $-r_A = k C_{A0}^2 (1-X)^2$

$-r_A = 10^{-2} k (1-X)^2$

6) Parameter Evaluation

A) CSTR $X = 0.85$ $T = 300 + 170 = 470$

$k = 4.31$, $k C_{A0}^2 = 0.0431$

$-r_A = (0.0431)(.15)^2 = 9.71 \times 10^{-4} \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}$

$V = \frac{F_{A0} X}{-r_A} = \frac{C_{A0} V_0 X}{-r_A} = \frac{(0.1)(2)(.85)}{9.71 \times 10^{-4}}$

$V = 175 \text{ dm}^3$

B) PFR

X	T	k	$-r_A \times 10^4$	$\frac{F_{A0}}{-r_A}$
0	300	0.01	1	$f_0 = 2000$
.2	340	.072	4.6	$f_1 = 435$
.4	380	.34	12.3	$f_2 = 163$
.6	420	1.21	19.3	$f_3 = 103$
.8	460	3.42	13.7	$f_4 = 146$
.85	470	4.31	9.71	$f_5 = 206$

$V = \frac{h}{3} [f_0 + 4f_1 + 2f_2 + 4f_3 + f_4] + \frac{h}{2} [f_4 + f_5]$

$= \frac{0.2}{3} [2000 + 4(435) + 2(163) + (103) + 146] + \frac{0.5}{2} [146 + 206]$

$= \frac{0.2}{3} [2000 + 1740 + 326 + 412 + 146] + \frac{0.5}{2} [146 + 206]$

$V = 308. + 8.8 = 317 \text{ dm}^3$

b) $T = T_o + \frac{(-\Delta H_R) X}{\sum \theta_i C_{Pi}}$

$550 = T_o + 200$

$T_o = 350$

P8-5 cont'd

c) POLYMATH

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

$$r_A = -k C_A^2$$

$$\frac{dT}{dV} = (r_A)(\Delta H_R) / (C_{pA} + C_{pB}) / F_{A0}$$

$$\Delta H_R = -6,000$$

$$k = 0.01 \exp \left[5032.7 \left(\frac{1}{300} - \frac{1}{T} \right) \right]$$

$$C_A = 0.1 (1-X)$$

$$F_{A0} = 0.2$$

d) POLYMATH CSTR

$$F(X) = 500 - \frac{2X}{-r_A}$$

$$r_A = -0.1 k (1-X)^2$$

$$k = 0.01 \exp \left[5033 \left(\frac{1}{300} - \frac{1}{T} \right) \right]$$

$$F(T) = 300 + 200X - T$$

$$X = .9, \quad T = 480, \quad k = 5.4$$

$$\text{Polymath } X = .9211 \quad T = 484.21$$

e) Making $E = 1000$, causes the conversion to decrease and the profile will be a straight line for the same volume. Making $E = 30000$ cause X to go to completion at a volume of only about 60 dm^3 . Making $\Delta H_R = -2000$ decreases the conversion and makes the profile a straight line. Making $\Delta H_R = -25000$ also causes the reaction to go to completion in a volume of only 45 dm^3 .

P8-5 cont'd

f) To find T_r , the following must be true:

$$T_r - T_c = \frac{RT_r^2}{E}$$

$$T_c = \frac{T_0 + \kappa T_A}{1 + \kappa} = \frac{300 + 3 \cdot 300}{1 + 3} = 300$$

So:

$$\frac{1.987}{10000} T_r^2 - T + 300 > 0$$

$$T_r > 320.4 K$$

P8-6

$$\frac{dX}{dW} = -r'_A / F_{A0}$$

$$\frac{dT}{dW} = \frac{r'_A \Delta H_R}{F_{A0} C_{pA}}$$

neglect pressure drop, $\epsilon = 1.0$

$$r_A = -k C_{A0} \frac{(1-X)}{(1+\epsilon X)} \frac{T_0}{T} = -k C_{A0} \frac{(1-X)}{(1+X)} \left(\frac{450}{T} \right)$$

$$C_{A0} = \frac{y_{A0} P_0}{RT_0} = \frac{(1)(10)}{(0.082)(450)} = 0.271 \frac{\text{mol}}{\text{dm}^3}$$

$$F_{A0} = v_0 C_{A0} = \left(\frac{20 \text{ dm}^3}{\text{s}} \right) \left(0.271 \frac{\text{mol}}{\text{dm}^3} \right) = 5.42 \frac{\text{mol}}{\text{s}}$$

$$E = \frac{31.4 \text{ kJ}}{\text{mol}} \cdot \frac{E}{R} = 3776.6$$

$$k = (1.33) \exp \left[3776.6 \left(\left(\frac{1}{450} \right) - \left(\frac{1}{T} \right) \right) \right]$$

$$\Delta C_p = 15 + 25 - 40 = 0$$

$$\Delta H_R = -40 + -50 - (-70) = -20 \frac{\text{kJ}}{\text{mol}}$$

Since the reaction is adiabatic, we could solve the energy balance to give

$$T = T_0 - \frac{\Delta H_R (T_0) X}{\sum \theta_i \bar{C}_{p,i} + X \Delta C_p}$$

P8-6 cont'd

$$T = T_0 - \frac{\Delta H_R X}{C_{Pa}}$$

$$T = 450 - \frac{(-20,000)X}{40}$$

$$T = 450 + 500 X$$

See POLYMATH Program Below

Problem

The equations:

$$d(x)/d(v) = -r_a / f_{aB}$$

$$d(t)/d(v) = r_a \cdot dh / (c_{pa} \cdot c_{pb}) / f_{aB}$$

$$k = .01 \cdot \exp(5032.7 \cdot (1/300 - 1/t))$$

$$c_{aB} = .1$$

$$c_a = c_{aB} \cdot (1 - x)$$

$$r_a = -k \cdot c_a = -2$$

$$dh = -6000$$

$$c_{pb} = 15$$

$$c_{pa} = 15$$

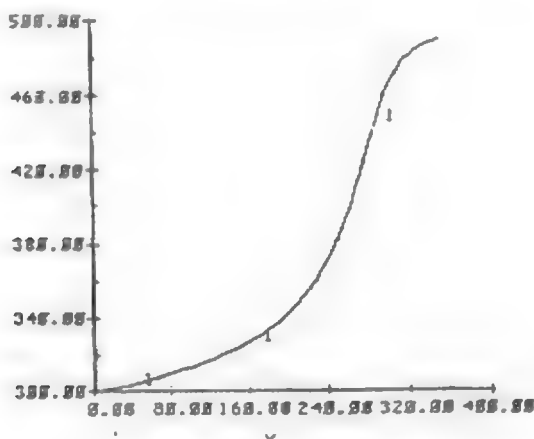
$$f_{aB} = .2$$

$$\text{rate} = -r_a$$

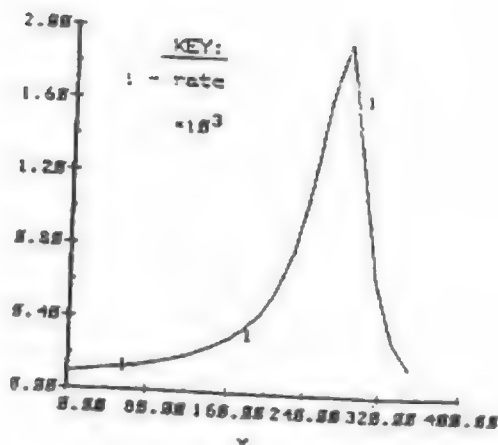
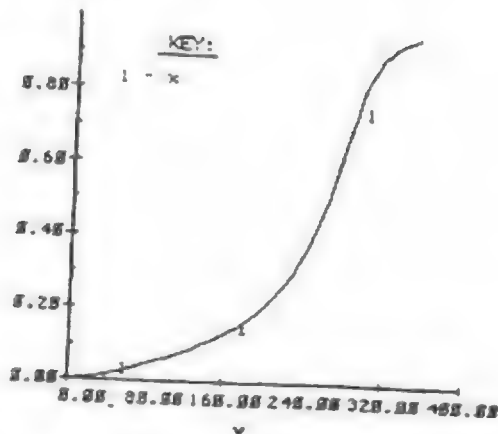
Initial values: $v_g = 0.0$, $x_g = 0.0$, $t_g = 300.00$

Final value: $v_f = 350.00$

KEY:
: - t



P8-6 cont'd



b) Fluidized bed CSTR

$$W = \frac{F_{A0}X}{-r_A}$$

$$-r_A = k C_{A0} \frac{(1-X)}{(1+\epsilon X)} \frac{T_0}{T}$$

$$k = (.133) \exp \left[3776.6 \left(\left(\frac{1}{450} \right) - \left(\frac{1}{T} \right) \right) \right]$$

Adiabatic with $\dot{W}_s = 0$

$$T = T_0 - \frac{\Delta H_R (T_0) X}{\sum \tilde{C}_p + X \Delta C_p}$$

$$\Delta H_R (T_R) = -20,000 \text{ kJ/mol}$$

$\Delta C_p = 0$, Pure A fed

$$T = T_0 + \frac{(-\Delta H_R (T_R)) X}{C_{pA}} = 450 + \frac{(-(-20,000))X}{40}$$

$$T = 450 + 500 X$$

when $X = .8$, $T = 850$

P8-6 cont'd

$$k = (.133) \exp \left[3776 \left(\frac{1}{450} - \frac{1}{850} \right) \right]$$

$$k = 6.9, \quad \varepsilon = 1$$

$$-r_A' = 6.9 (0.271) \frac{(1-.8)}{(1+.8)} \frac{450}{850} = 0.11 \text{ mol/kg cat-s}$$

$$W = \frac{(5.42 \text{ mol/s})(.8)}{.11 \text{ mol/kg cat-s}} = 39.4 \text{ kg cat}$$

problem 8-6

The equations:

$$d(x)/d(w) = -r_A'/f_{A0}$$

$$t_1 = 458.588 * x$$

$$k = .133 * \exp(3776.6 * ((1/458) - (1/t_1)))$$

$$C_{A0} = .271$$

$$C_A = C_{A0} * (1-x) = (458/t_1) / (1+x)$$

$$r_A = -k * C_A$$

$$f_{A0} = 5.42$$

$$dhr = -28888$$

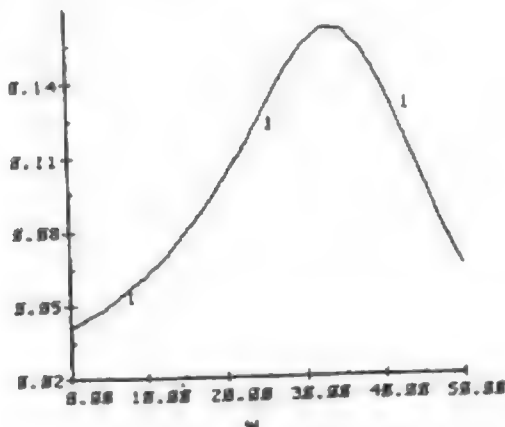
$$C_{D0} = 18$$

$$rate = -r_A$$

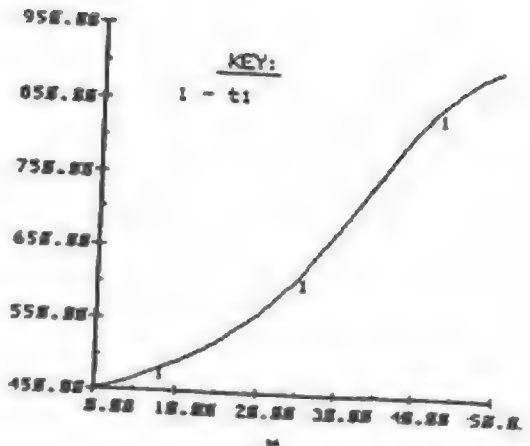
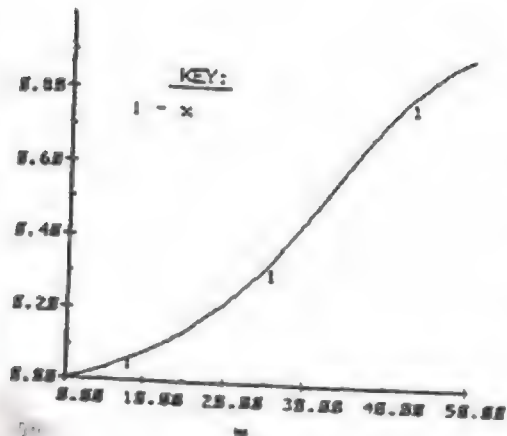
Initial values: $w_0 = 0.0, x_0 = 0.0$

Final value: $w_f = 58.888$

KEY:
1 = rate



P8-6 cont'd



P8-7

$$\frac{dX}{dW} = \frac{-r'_A}{F_{A0}}$$

$$\frac{dT}{dW} = \frac{r'_A (\Delta H_R)}{F_{A0} C_{pA}}$$

or since reaction is adiabatic with $\dot{W}_S = 0$ we could use

$$T = 450 + 500 X$$

$$-r'_A = k C_{A0} \frac{(1-X)}{(1+X)} \left(\frac{450}{T} \right) y$$

where $y = P/P_0$

Then

$$\frac{dy}{dW} = - \frac{\alpha (1+X) (T/T_0)}{2y} = - \frac{\alpha (1+X)}{2y} \left(\frac{T}{450} \right)$$

$$k = \left(\frac{0.133}{s} \right) \exp \left[3776.6 \left(\left(\frac{1}{450} \right) - \left(\frac{1}{T} \right) \right) \right]$$

See POLYMATH Program $-r'_A = k C_{A0} = 0.27 \frac{\text{mol}}{\text{dm}^3} \cdot \text{s}$, $F_{A0} = 5.42 \frac{\text{mol}}{\text{s}}$, $\alpha = 0.019 \text{ kg}^{-1}$

adiabatic pbr with pressure drop

The equations:

$$d(x)/d(w) = -ra/fa\beta$$

$$d(t1)/d(w) = ra \cdot dhr / (fa\beta \cdot cpa)$$

$$d(y)/d(w) = -(1+x) \cdot (t1/458) \cdot \alpha / (2+y)$$

$$k = .139 \cdot \exp(3776.6 \cdot ((1/458) - (1/t1)))$$

$$ca\beta = .271$$

$$ca = ca\beta \cdot (1-x) \cdot (458/t1) / (1+x) \cdot y$$

$$ra = -k \cdot ca$$

$$fa\beta = 5.42$$

$$dhr = -28888$$

$$cpa = 48$$

$$rate = -ra$$

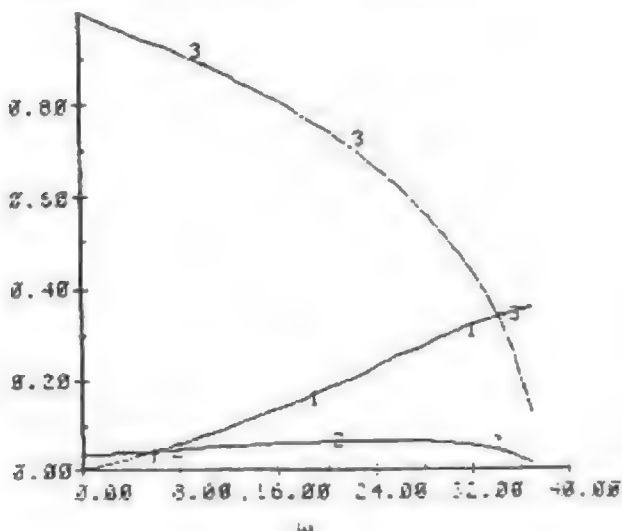
$$\alpha = .819$$

Initial values: $w_0 = 0.8$, $x_0 = 0.8$, $t1_0 = 458.88$, $y_0 = 1.3888$ Final value: $w_f = 37.888$

adiabatic pbr with pressure drop

KEY:

- 1 - x
- 2 - rate
- 3 - y



adiabatic por
Integration Results

<u>w</u>	<u>x</u>	<u>t1</u>	<u>rate</u>	<u>y</u>
1.5000	0.0101	450.00	0.0360	1.0000
3.5000	0.0237	455.05	0.0378	0.9056
4.5000	0.0310	460.34	0.0396	0.9787
5.0000	0.0434	465.89	0.0416	0.9552
7.5000	0.0556	471.71	0.0436	0.9392
1.0000	0.0684	477.01	0.0457	0.9224
10.5000	0.0810	484.20	0.0473	0.9049
12.0000	0.0950	490.89	0.0500	0.8866
13.5000	0.1104	497.89	0.0523	0.8674
15.0000	0.1256	505.20	0.0545	0.8472
		512.82	0.0567	0.8259

<u>w</u>	<u>x</u>	<u>t1</u>	<u>rate</u>	<u>y</u>
15.0000	0.1256	512.82	0.0567	0.8259
16.5000	0.1415	520.74	0.0589	0.8035
18.0000	0.1579	528.96	0.0609	0.7797
19.5000	0.1749	537.44	0.0626	0.7544
21.0000	0.1923	546.16	0.0641	0.7275
22.5000	0.2102	555.00	0.0653	0.6986
24.0000	0.2283	564.14	0.0659	0.6676
25.5000	0.2465	573.26	0.0659	0.6341
27.0000	0.2647	582.36	0.0652	0.5976
28.5000	0.2825	591.27	0.0634	0.5566
30.0000	0.2997	599.86	0.0606	0.5109

adiabatic pbr

Integration Results

<u>w</u>	<u>x</u>	<u>t1</u>	<u>rate</u>	<u>v</u>
38.888	8.2997	599.86	8.8686	8.5189
38.388	8.3031	601.53	8.8599	8.5212
38.688	8.3064	603.19	8.8591	8.4912
38.988	8.3096	604.82	8.8583	8.4910
31.288	8.3128	606.42	8.8574	8.4785
31.588	8.3168	608.08	8.8564	8.4597
31.888	8.3191	609.56	8.8554	8.4486
32.188	8.3222	611.09	8.8544	8.4372
32.488	8.3252	612.58	8.8532	8.4254
32.788	8.3281	614.05	8.8528	8.4132
33.088	8.3318	615.48	8.8587	8.4086
33.388	8.3337	616.87	8.8493	8.3875
33.688	8.3364	618.22	8.8478	8.3739
33.988	8.3391	619.53	8.8462	8.3598
34.288	8.3416	620.88	8.8445	8.3458
34.588	8.3448	622.02	8.8427	8.3295
34.888	8.3464	623.19	8.8488	8.3132
35.188	8.3486	624.38	8.8337	8.2968
35.488	8.3507	625.36	8.8364	8.2777
35.788	8.3527	626.35	8.8348	8.2581
36.088	8.3546	627.27	8.8313	8.2369

<u>w</u>	<u>x</u>	<u>t1</u>	<u>rate</u>	<u>v</u>
36.888	8.3546	627.27	8.8313	8.2369
36.875	8.3558	627.49	8.8305	8.2311
36.158	8.3554	627.78	8.8298	8.2253
36.225	8.3558	627.98	8.8298	8.2193
36.388	8.3562	628.18	8.8282	8.2131
36.375	8.3566	628.38	8.8274	8.2067
36.458	8.3578	628.48	8.8265	8.2081
36.525	8.3573	628.67	8.8256	8.1933
36.688	8.3577	628.84	8.8247	8.1862
36.675	8.3588	629.01	8.8238	8.1789
36.758	8.3584	629.17	8.8228	8.1713
36.825	8.3587	629.33	8.8217	8.1633
36.988	8.3598	629.48	8.8206	8.1549
36.975	8.3592	629.62	8.8194	8.1468
37.858	8.3595	629.75	8.8182	8.1366
37.125	8.3598	629.87	8.8168	8.1264
37.288	8.3608	629.99	8.8154	8.1155
37.275	8.3602	630.09	8.8138	8.1034
37.358	8.3604	630.18	8.8128	8.8898
37.425	8.3605	630.26	8.987 × 10 ⁻²	8.8748
27.588	8.3607	630.32	8.781 × 10 ⁻²	8.8526

P8-8 Same as 8-6 except for the energy balance

$$\frac{dX}{dW} = -r_A' / F_{A0}$$

$$\frac{dT}{dW} = \frac{[(U_s / \rho C) (T_s - T) + (r_A') (\Delta H_R)]}{F_{A0} \sum \theta_i C_{Pi}}$$

$$\frac{dT}{dW} = \frac{[(U_s / \rho C) (T_s - T) + (r_A') (\Delta H_R)]}{F_{A0} C_{pA}}$$

$$U_s / \rho C = 0.8 \text{ J/s} \cdot \text{kg cat} \cdot \text{K}$$

$$T_s = 323 \text{ K}$$

Other variables the same P8-6

For Parts (a), (b), and (c)

$$r_A = -k C_{A0} \frac{(1-X)}{(1+X)} \left(\frac{450}{T} \right)$$

For Part (d)

$$r_A = -k C_{A0} \frac{(1-X)}{(1+X)} \frac{450}{T} + \frac{k_r C_{A0}^2 X^2}{(1+X)^2} \left(\frac{450}{T} \right)^2$$

This system of equations must be solved numerically. See POLYMATH Program and results.

for w heat exchange

(a) The equations:

$$d(x)/d(w) = -r_A / f_{A0}$$

$$d(t_1)/d(w) = (u_s (t_s - t_1) + r_A \Delta H_R) / (f_{A0} \rho C_p)$$

$$k = 133 \cdot \exp(3776.6 \cdot ((1/450) - (1/t_1)))$$

$$C_{A0} = .271$$

$$C_A = C_{A0} (1-x) = (450/t_1) / (1+x)$$

$$r_A = -k C_A$$

$$f_{A0} = 5.42$$

$$\Delta H_R = -28888$$

$$C_{pA} = 40$$

$$\text{rate} = -r_A$$

$$u_s = .3$$

$$t_s = 323$$

Initial values: $w_0 = 0.0$, $x_0 = 0.0$, $t_{10} = 450.00$
 Final value: $w_f = 50.000$

Integration Results

<u>w</u>	<u>x</u>	<u>t1</u>	<u>rate</u>
0.0	0.0	458.88	0.0368
2.5000	0.0170	457.30	0.0392
5.0000	0.0355	465.20	0.0428
7.5000	0.0556	474.85	0.0469
10.0000	0.0783	483.95	0.0516
12.5000	0.1034	494.93	0.0571
15.0000	0.1311	507.15	0.0633
17.5000	0.1618	520.77	0.0703
20.0000	0.1961	535.90	0.0782
22.5000	0.2341	552.95	0.0869
25.0000	0.2763	571.84	0.0962

pbr w heat exchange

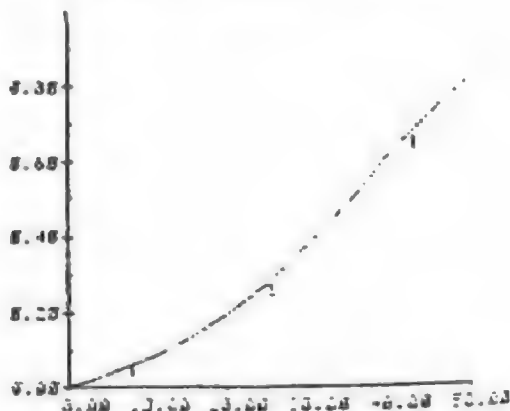
Integration Results

<u>w</u>	<u>x</u>	<u>t1</u>	<u>rate</u>
25.0000	0.2763	571.84	0.0962
27.5000	0.3223	592.73	0.1057
30.0000	0.3737	615.50	0.1140
32.5000	0.4285	640.10	0.1226
35.0000	0.4865	666.10	0.1281
37.5000	0.5459	692.50	0.1381
40.0000	0.6050	719.84	0.1280
42.5000	0.6635	744.14	0.1216
45.0000	0.7174	767.11	0.1117
47.5000	0.7662	787.30	0.0994
50.0000	0.8089	804.31	0.0859

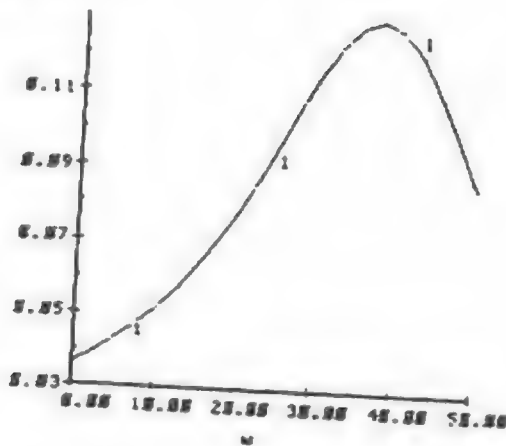
pbr w heat exchange

(a)

KEY:
1 - x

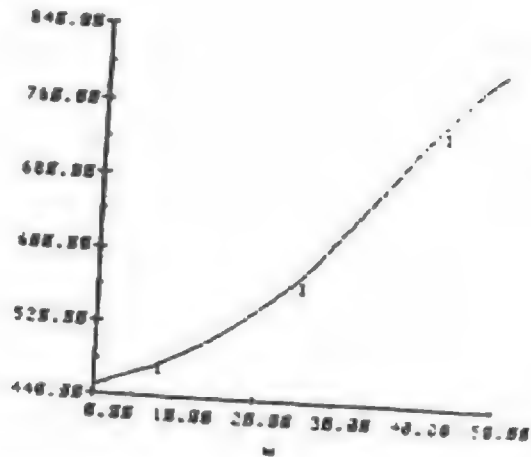


P8-8 cont'd



KEY:
1 - rate

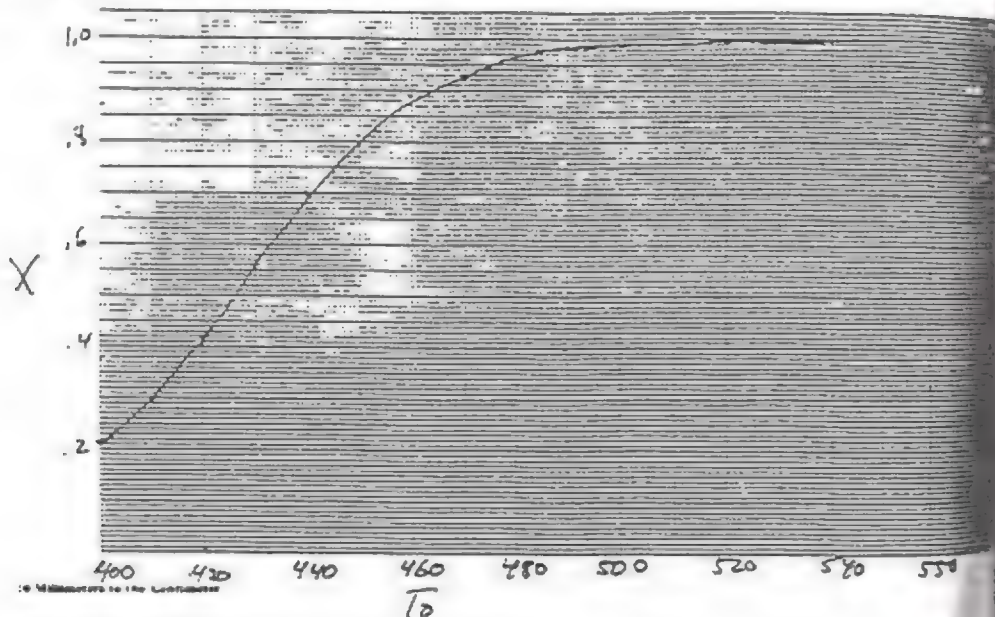
KEY:
1 - t_1



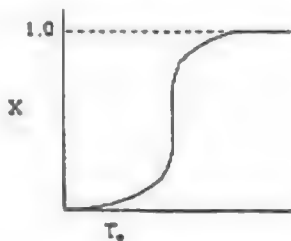
P8-9 (b) Conversion as a function of entering temperature.

$T_0 = 400$	$X = .22$	$T_0 = 450$	$X = .31$
$T_0 = 410$	$X = .30$	$T_0 = 460$	$X = .38$
$T_0 = 420$	$X = .42$	$T_0 = 470$	$X = .925$
$T_0 = 430$	$X = .56$	$T_0 = 500$	$X = .979$
$T_0 = 440$	$X = .70$	$T_0 = 550$	$X = .996$

P8-8 cont'd



Because the activation energy and heat of reaction are not particularly large there is not a particularly large jump in temperature with entering temperature. For large E and ΔH_R one might find.



P8-8 (c)

$$UA(T_o - T) - F_{A0} \sum \theta_i \bar{C}_{pi} (T - T_o) - F_{A0} X (\Delta H_R) = 0$$

$$UA(T_o - T) - F_{A0} C_{pA} (T - T_o) - F_{A0} X (\Delta H_R) = 0$$

$$500(323 - T) - 5.42(40)(T - 450) - 5.42(0.8)(20000) = 0$$

$$T = 482.9$$

$$W = 655.9$$

P8-8 cont'd

CSTR

(c) The equations:

$$f(v) = v - f_{aB} \cdot v, \quad i - r_B$$

$$t = 462.9$$

$$h = .133 \cdot \exp(3776.6 \cdot (1/458 - 1/t))$$

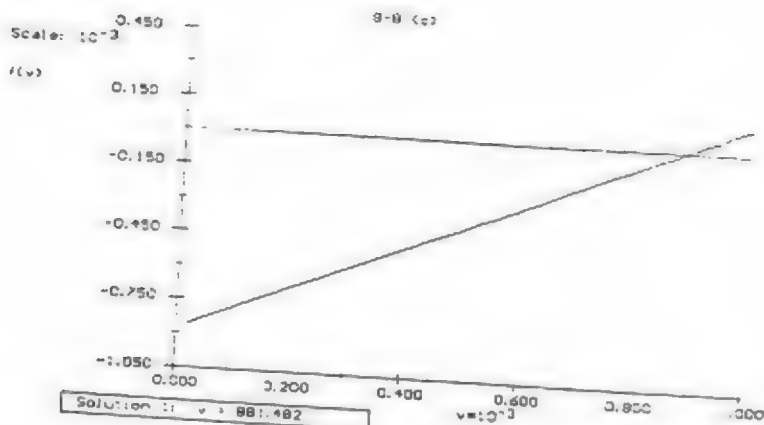
$$-ca_B = .271$$

$$x = .8$$

$$r_B = -h \cdot ca_B \cdot (1-x) = 458 / (t \cdot (1-x))$$

$$f_{aB} = 5.42$$

Search range: $v_{\min} = 28.888, v_{\max} = 1888.8$



P8-8 cont'd

P8-8 (d) Repeat Part 8-8(a) for $W = 80$ kg and assuming a reversible reaction with a reverse specific reaction rate of

$$k_r = 0.2 \exp \left(\frac{E}{R} \left[\frac{1}{450} - \frac{1}{T} \right] \right) \left(\frac{dm^6}{\text{kg cal} \cdot \text{mol} \cdot \text{s}} \right) E = 51.4 \frac{\text{kJ}}{\text{mol}}$$

per w heat exchange and reverse rxn

The equations:

$$d(x)/dw = -ra/5.42$$

$$d(t1)/dw = (ua \cdot (ta - t1) + ra \cdot dhr) / (5.42 \cdot cpa)$$

$$k = 1.33 \cdot \exp(3776.6 \cdot ((1/450) - (1/t1)))$$

$$caB = .271$$

$$ca = caB \cdot (1 - x) = (450/t1) / (1 + x)$$

$$kr = .2 \cdot \exp(6195.3 \cdot ((1/450) - (1/t1)))$$

$$ra = -k \cdot ca - kr = (caB \cdot x \cdot (450/t1) / (1 + x)) \cdot 2$$

$$dhr = -28388$$

$$cpa = 49$$

$$rate = -ra$$

$$ua = .3$$

$$ta = 322$$

Initial values: $w_0 = 8.8$, $x_0 = 0.0$, $t1_0 = 450.89$

Final value: $w_f = 38.888$

Integration Results

<u>w</u>	<u>x</u>	<u>rate</u>	<u>t1</u>
25.888	0.2681	0.8869	567.33
27.588	0.3087	0.8987	585.83
30.888	0.3587	0.8917	604.39
32.588	0.3923	0.8889	622.79
35.888	0.4324	0.8828	639.73
37.588	0.4608	0.8719	654.54
40.888	0.4934	0.8681	666.66
42.588	0.5234	0.8481	675.98
45.888	0.5438	0.8374	682.44
47.588	0.5581	0.8235	686.65
50.888	0.5696	0.8216	689.82

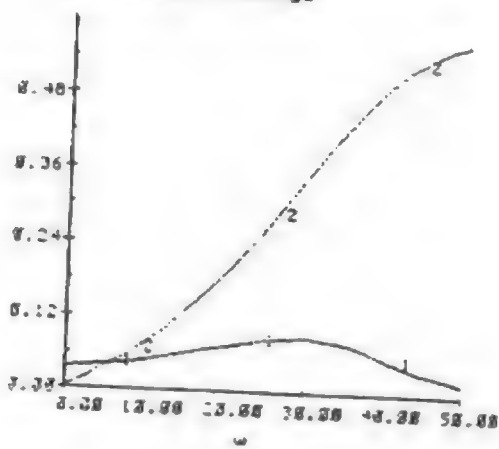
por w heat exchange

Integration Results

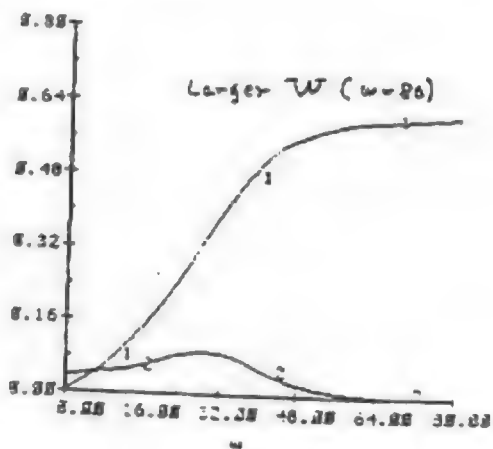
θ	η	rate	τ
0.0	0.0	0.0368	458.88
2.5000	0.0178	0.0392	457.32
5.0000	0.0255	0.0422	465.22
7.5000	0.0353	0.0458	474.83
10.000	0.0477	0.0513	493.86
12.500	0.1025	0.0565	494.55
15.000	0.1299	0.0622	506.59
17.500	0.1488	0.0685	519.32
20.000	0.1931	0.0752	534.56
22.500	0.2092	0.0814	550.59
25.000	0.2131	0.0869	567.33

por w heat exchange

KEY:
1 - rate
2 - η



KEY:
1 - η
2 - rate



P8-8 cont'd

e) The lower Ua/p_c is the higher the temperature gets and the bigger the conversion gets. For example when the quantity equals 0.1, $X = 0.9$ and $T = 891\text{K}$. When the quantity equals 20, $X = 0.06$ and $T = 326.7\text{K}$. As for the ambient temperature change, in a northern state in the winter, ($T_a = 266\text{K}$), the conversion falls to .78 and the temperature falls to 778K. In the summer ($T = 305\text{K}$), the conversion is at 0.8 while the temperature of the reactor goes to 797.1K. As you can see the ambient temperature of the seasons does not change the usefulness of the reactor that much.

f) If pressure drop were included the combined temperature and pressure might make the reactor unuseable as it might build up too much.

g) No solution will be given.

P8-9



a) Design equation:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

Rate law:

$$-r_A = kC_A^2$$

Stoichiometry:

$$C_A = C_{A0}(1 - X)$$

Energy balance:

$$\frac{dT}{dV} = \frac{Ua(T_A - T) + (-r_A)(- \Delta H_{RX})}{F_{A0}C_{pA}}$$

$$\frac{dT}{dV} = \frac{5(700 - T) + (231 + .012(T - 298))(-r_A)}{5 \cdot .122}$$

Plugging those into POLYMATH gets the following program and the following graphs. The conversion achieved is 0.36.

8-9

Equations:

$$d(T)/d(V) = (Ua \cdot (Ta - T) + (-ra) \cdot (-Dhr)) / (fao \cdot cpa)$$

$$d(x)/d(V) = -ra/fao$$

$$fao = 5$$

$$Ua = 5$$

$$Ta = 700$$

$$Dhr = -231 - .012 \cdot (T - 298)$$

$$cpa = .1222$$

$$k = 1.48e11 \cdot \exp(-19124/T)$$

$$cao = 1$$

$$ca = cao \cdot (1 - x)$$

$$ra = -k \cdot ca^2$$

$$v_0 = 0. \quad v_f = 10$$

Initial value

675

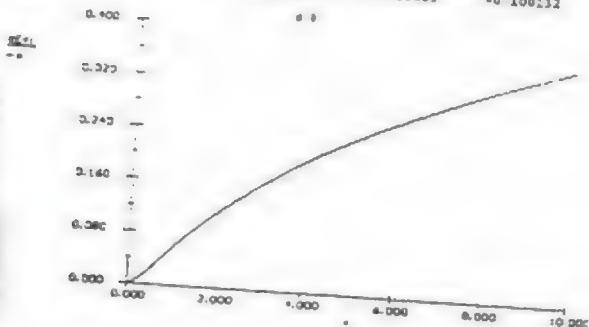
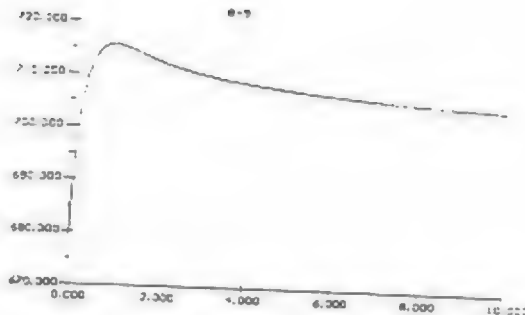
0

8-27

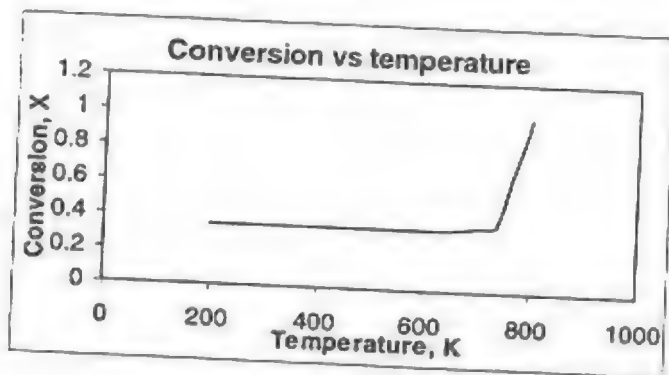
P8-9 cont'd

8-9

Variable	Initial value	Maximum value	Minimum value	Final value
v	0	10	0	10
T	675	715.56	675	704.769
x	0	0.358088	0	0.358088
foo	5	5	5	5
Da	5	5	5	5
Ta	700	700	700	700
Dir	-235.524	-235.524	-236.011	-235.881
cpe	0.1222	0.1222	0.1222	0.1222
k	0.0734336	0.365882	0.0734336	0.243008
cao	1	1	1	1
ca	1	1	1	1
ca	-0.0734336	-0.0734336	-0.333623	-0.641912



b) Using the same POLYMATH program we were able to change the entering temperature and come up with this graph.



c) Again using the same POLYMATH program, we can vary the ambient temperature until the reaction runs away. As the following summary table will show the maximum temperature is 708 K.

P8-9 cont'd

8-9

Variable	Initial value	Maximum value	Minimum value	Final value
v	0	10	0	10
T	675	758.054	675	712.267
x	0	0.486285	0	0.486285
fao	5	5	5	5
Ua	5	5	5	5
Ta	708.2	708.2	708.2	708.2
Dhr	-235.524	-235.524	-234.522	-235.971
cpa	0.1222	0.1222	0.1222	0.1222
k	0.0734336	1.63679	0.0734336	0.32335
cao	1	1	1	1
ca	1	1	0.513715	0.513715
ra	-0.0734336	-0.0734336	-1.07779	-0.0853333

d) When the reaction becomes adiabatic the energy balance will then become:

$$T = T_0 + \frac{(-r_A)(-\Delta H_R)}{C_{pA}}$$

However, the heat of reaction is a function of temperature. This is a circular reference, so we need to find T as a function of just X.

$$T = \frac{T_0 C_{pA} - 231X - 3.576X}{C_{pA} - 0.012X}$$

Plugging that into POLYMATH gets the following program and graphs.

8-9

Equations:

d(x)/d(v) = -ra/fao

Ua=5

fao=5

Ta=708.2

cpa=.1222

cao=1

To=675

ca=cao*(1-x)

T=(To*cpa-231*x-3.576*x)/(cpa-.012*x)

k=1.48e11*exp(-19124/T)

Dhr=-231-.012*(T-298)

ra=-k*ca^2

v0 = 0, v_f = 10

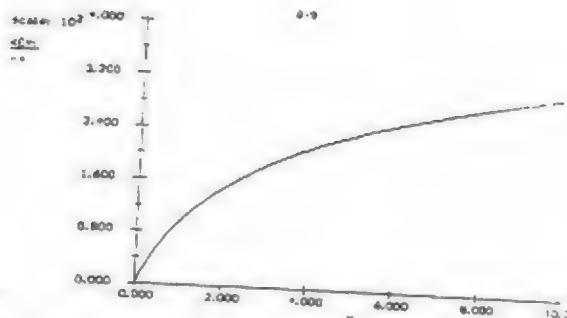
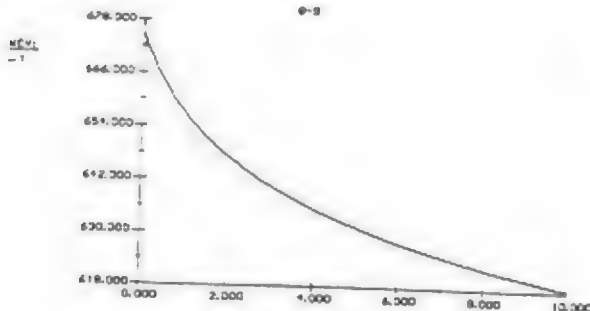
Initial value

0

8-9

Variable	Initial value	Maximum value	Minimum value	Final value
v	0	10	0	10
x	0	0.0304837	0	0.2304837
Ua	5	5	5	5
fao	5	5	5	5
Ta	708.2	708.2	708.2	708.2
cpa	0.1222	0.1222	0.1222	0.1222
cao	1	1	1	1
To	675	675	675	675
ca	1	1	0.969516	0.969516
T	675	675	618.134	618.134
k	0.0734336	0.0734336	0.0054738	0.0054738
Dhr	-235.524	-234.844	-235.524	-234.844
ra	-0.0734336	-0.00514516	-0.0734336	-0.00514516

P8-9 cont'd



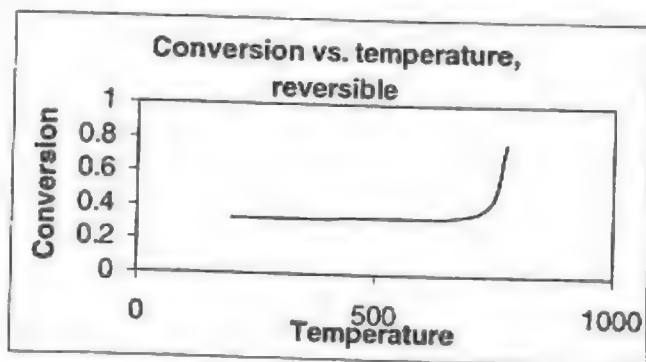
e) When it becomes reversible with inerts the two equations that change are the rate law and the energy balance.

$$-r_A = k \left(C_A^2 - \frac{C_B}{K} \right)$$

$$\frac{dT}{dV} = \frac{Ua(T_A - T) + (-r_A)(-\Delta H_R)}{F_{A0}(C_{pA} + \Theta_i C_{pi})}$$

$$K = 100000 \exp \left[\frac{\Delta H_R}{R} \left(\frac{1}{675} - \frac{1}{T} \right) \right]$$

We can use those equations in POLYMATH and the following graph is made:



There is no maximum because the reaction is a runaway at a certain temperature and the conversion goes to close to one at that point.

f) No solution will be given.

a)

$$C_A = C_T \frac{F_A}{F_T}$$

$$\theta = \frac{F_I}{F_A}$$

$$C_T = C_A + C_I$$

$$F_T = F_A + F_I$$

$$\frac{1}{C_A} = \frac{1}{C_A + C_I} \frac{F_I + F_A}{F_A}$$

$$\frac{1}{C_A} = \frac{1}{C_A + C_I} (\theta_I + 1)$$

$$C_A = \frac{C_A + \frac{P_I}{RT}}{(\theta_I + 1)}$$

where $\theta_I = \frac{F_I}{F_A}$

b) Mole balance:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

$$-r_A = kC_A$$

$$k = \exp(34.4 - 34.222/T)$$

$$\epsilon = \frac{1}{\theta_I + 1}$$

$$C_A = C_{A0} \frac{1-X}{1+\epsilon X}$$

$$-r_A = k \left[\frac{\frac{C_{A0} + C_I}{\theta_I + 1} (1-X)}{1 + \left(\frac{1}{\theta_I + 1} \right) X} \right]$$

$$T = \frac{X(-80000) + C_{pA}T_0 + \theta_I C_{pI}T_0}{C_{pA} + \theta_I C_{pI}}$$

Plugging into POLYMATH gives the following.

P8-10 cont'd

8-10

Equations:

$$d(x)/d(v) = -r_a / f_{ao}$$

$$c_{ao} = 0.022$$

$$f_{ao} = 10$$

$$\theta = 0.1$$

$$c_{io} = 2 / .082 / 1100$$

$$T = (x \cdot -80000 + 170 \cdot 1100 + \theta \cdot 200 \cdot 1100) / (170 + \theta \cdot 200)$$

$$k = \exp(34.34 - 34222/T)$$

$$r_a = -k \cdot ((c_{ao} + c_{io}) / (\theta + 1)) \cdot (1-x) / (1+x / (\theta + 1))$$

$$v_0 = 0, \quad v_f = 500$$

Initial value

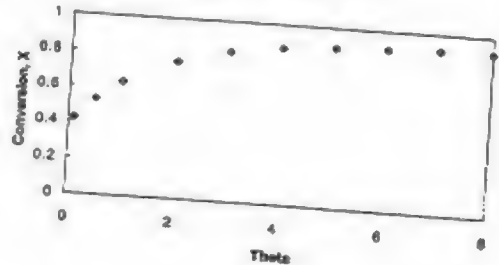
0

8-10

Variable

Variable	Initial value	Maximum value	Minimum value	Final value
v	0	500	0	500
x	0	0.420529	0	0.420529
c _{ao}	0.022	0.022	0.022	0.022
f _{ao}	10	10	10	10
θ	0.1	0.1	0.1	0.1
c _{io}	0.0221729	0.0221729	0.0221729	0.0221729
T	1100	1100	922.935	922.935
k	25.2567	25.2567	0.0646006	0.0646006
r _a	-1.01424	-0.0010875	-1.01424	-0.0010875

Conversion vs theta



- c) There is a maximum at about a theta of 8. This is due to the fact that there is so much more inert in the reactor than reactants.
- d) Increasing the temperature by 200k causes the reaction to go to completion at a very low theta. Decreasing the temperature has the opposite effect and the conversion will drop dramatically.
- e) No solution will be given.

P8-11

- a) Start with the complete energy balance:

$$\frac{d\dot{E}_{sys}}{dt} = \dot{Q} - \dot{W}_s - \sum_{i=1}^n E_i F_i |_{in} - \sum_{i=1}^n E_i F_i |_{out} - \sum_{i=1}^n R_i V E_i |_{out}$$

The following simplifications can be made:

- 1) It is at steady-state.
- 2) In part a, there is no heat added or taken away.
- 3) There is no shaft work.

That leaves us with the following:

$$0 = - \sum_{i=1}^n E_i F_i |_{in} - \sum_{i=1}^n E_i F_i |_{out} - \sum_{i=1}^n R_i V E_i |_{out}$$

P8-11 cont'd

Evaluating the energy terms:

$$\text{In: } H_{A0}F_{A0} + H_{B0}F_{B0} + H_{C0}F_{C0}$$

$$\text{Out: } H_A(F_A + R_A V) + H_B(F_B + R_B V) + H_C(F_C + R_C V)$$

Simplifying again:

$$-F_{A0}[(H_{A0} - H_A) + (H_{B0} - H_B)\phi_B + (H_{C0} - H_C)\phi_C] - \Delta H_{RX}F_{A0}X - \Delta H_{RX}R_B V = 0$$

$$-F_{A0} \sum_{i=1}^n \theta_i C_{pi} (T - T_i) - F_{A0} X \left[\Delta H_{RX}(T) + \int_{T_A}^T \Delta C_p dT \right] - \sum_{i=1}^n R_i V \left[\Delta H_{RX}(T) + \int_{T_B}^T \Delta C_p dT \right] = 0$$

Differentiating with respect to V with $\Delta C_p = 0$:

$$-F_{A0} \sum_{i=1}^n \theta_i C_p \frac{dT}{dV} - F_{A0} \frac{dX}{dV} (\Delta H_{RX}(T)) - \sum_{i=1}^n R_i [\Delta H_{RX}(T)]$$

$$\frac{dT}{dV} = \frac{F_{A0}(-r_A)[\Delta H_{RX}(T)] + \sum_{i=1}^n R_i [\Delta H_{RX}(T)]}{F_{A0} \sum_{i=1}^n \theta_i C_p}$$

Combine that with the following mole balances and rate law:

$$\frac{dF_A}{dV} = r_A \quad \frac{dF_B}{dV} = -r_A \quad \frac{dF_C}{dV} = -r_A - k_c C_C$$

$$-r_A = k C_A$$

$$C_A = C_{T0} \frac{F_A T_0}{F_T T} \quad C_B = C_{T0} \frac{F_B T_0}{F_T T} \quad C_C = C_{T0} \frac{F_C T_0}{F_T T}$$

Plug them into POLYMATH and get the following program and graphs for different values of k_c .

Equations:

$$d(fb)/d(v) = -ra$$

$$d(fa)/d(v) = ra$$

$$d(fc)/d(v) = -ra - kc*cc$$

$$d(T)/d(v) = (fao*(-ra)*(-Dhrl) + Rc*(-Dhrl))/(fao*cpa)$$

$$kc=10$$

$$Dhrl=-20000$$

$$cpa=40$$

$$To=450$$

$$E=31400$$

$$R=8.31$$

$$cto=10/(.082*To)$$

$$k=.133*\exp(E/R*(1/450-1/T))$$

$$fao=cto*20$$

$$ft=fao$$

$$cc=cto*fc/ft*To/T$$

$$ca=cto*fa/ft*To/T$$

$$cb=cto*fb/ft*To/T$$

$$Rc=kc*cc$$

$$ra=-k*ca$$

$$v_0 = 0, \quad v_f = 30$$

initial value

0

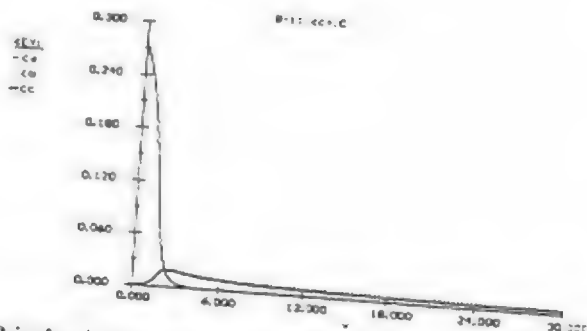
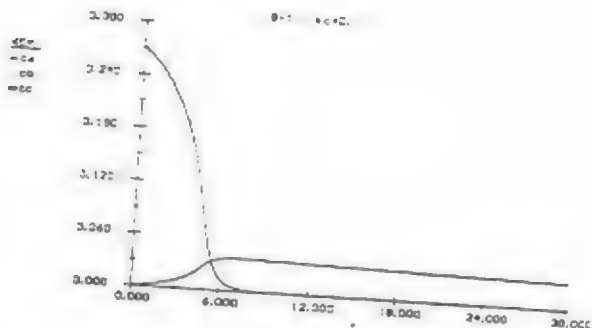
5.42

0

450

Variable	Initial value	Maximum value	Minimum value	Final value
v	0	30	0	30
fb	0	5.42	0	5.42
fa	5.42	5.42	7.38118e-14	7.38118e-14
fc	0	4.13013	0	1.01336
T	450	3566.51	450	3566.51
kc	10	10	10	10
Dhrl	-20000	-20000	-20000	-20000
cpa	40	40	40	40
To	450	450	450	450
E	31400	31400	31400	31400
R	8.31	8.31	8.31	8.31
cto	0.271003	0.271003	0.271003	0.271003
k	0.131	204.379	0.131	204.379
fao	5.42005	5.42005	5.42005	5.42005
ft	5.42005	5.42005	5.42005	5.42005
cc	0	0.0307012	0	0.00639295
ca	0.271	0.271	4.65656e-16	4.65656e-16
cb	0	0.0371587	0	0.0341931
Rc	0	0.107012	0	0.0039295
ra	-0.036243	-9.51704e-14	-2.53479	-9.51704e-14

P8-11 cont'd



b) The only difference in B is that in the energy balance a heat term is added:

$$\frac{dT}{dV} = \frac{Ua(T_o - T) + F_{A0}(-r_A)(\Delta H_{rx}(T)) + \sum_{i=1}^n R_i[\Delta H_{f,i}(T)]}{F_{A0} \sum_{i=1}^n \theta_i C_{p,i}}$$

Plug this into POLYMATH and the following program and graphs are generated:

P8-11 cont'd

Equations:

$$d(fb)/d(v) = -ra$$

$$d(fa)/d(v) = ra$$

$$d(fc)/d(v) = -ra - kc \cdot cc$$

$$d(T)/d(v) = (Ua \cdot (Ta - T) + fao \cdot (-ra) \cdot (-Dhrl) + Rc \cdot (-Dhrl)) / (fao \cdot cpa)$$

$$kc = .1$$

$$Dhrl = -20000$$

$$cpa = 40$$

$$To = 450$$

$$E = 31400$$

$$R = 8.31$$

$$Ua = .8$$

$$Ta = 323$$

$$cto = 10 / (.082 \cdot To)$$

$$k = .133 \cdot \exp(E/R \cdot (1/450 - 1/T))$$

$$fao = cto \cdot 20$$

$$ft = fao$$

$$cc = cto \cdot fc / ft \cdot To / T$$

$$ca = cto \cdot fa / ft \cdot To / T$$

$$cb = cto \cdot fb / ft \cdot To / T$$

$$Rc = kc \cdot cc$$

$$ra = -k \cdot ca$$

$$v_0 = 0, \quad v_f = 30$$

Initial value

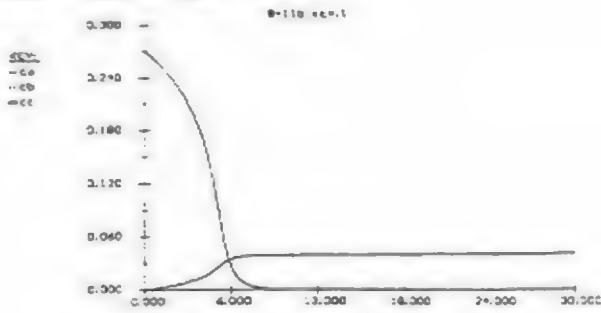
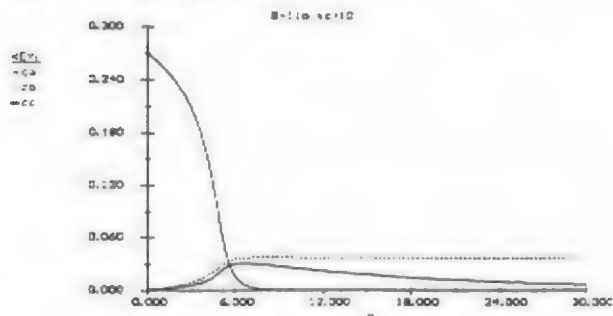
0

5.42

0

450

Variable	Initial value	Maximum value	Minimum value	Final value
v	0	30	0	30
fb	0	5.42	0	5.42
fa	5.42	5.42	2.2186e-13	2.2186e-13
fc	0	5.38932	0	5.31801
T	450	3107.16	450	2924.6
kc	0.1	0.1	0.1	0.1
Dhrl	-20000	-20000	-20000	-20000
cpa	40	40	40	40
To	450	450	450	450
E	31400	31400	31400	31400
R	8.31	8.31	8.31	8.31
Ua	0.8	0.8	0.8	0.8
Ta	323	323	323	323
cto	0.271003	0.271003	0.271003	0.271003
k	0.133	174.749	0.133	161.975
fao	5.42005	5.42005	5.42005	5.42005
ft	5.42005	5.42005	5.42005	5.42005
cc	0	0.0409133	0	0.0409133
ca	0.271	0.271	1.70684e-15	1.70684e-15
cb	0	0.0416979	0	0.0416979
Rc	0	0.00409133	0	0.00409133
ra	-0.036043	-2.76466e-13	-2.45733	-2.76466e-13



a) Energy balance

$$\frac{dT}{dW} = \frac{Ua/\rho_b(T_s - T) + (-r_A)[-\Delta H_R(T_R)]}{F_{A0}(\sum \theta_i C_{pi} + X\Delta C_p)}$$

$$\frac{dT}{dW} = \frac{Ua/\rho_b(T_s - T) + (-r_A)[-\Delta H_R(T_R)]}{F_{A0}C_{pA}}$$

Mole balance: $\frac{dX}{dW} = \frac{-r_A}{F_{A0}}$

Pressure drop: $\frac{dy}{dW} = \frac{-\alpha}{2y} \frac{T_0}{T} (1 + X)$

Rate law: $-r_A = kC_A$

Stoichiometry: $C_A = C_{A0} \left(\frac{1-X}{1+X} \right) \left(\frac{T}{T_0} \right)^y$

Evaluating the parameters: $k = \exp \left[\frac{E}{R} \left(\frac{1}{450} - \frac{1}{T} \right) \right] = \exp \left[3776.76 \left(\frac{1}{450} - \frac{1}{T} \right) \right]$

Plugging these equations into POLYMATH we get the following plots.

Equations:

$$d(y)/d(w) = -a/(2*y) * (T_0/T) * (1+x)$$

$$d(T)/d(w) = (U*(T_s - T) - r_A * dh) / f_{A0} / c_{pA}$$

$$d(x)/d(w) = -r_A / f_{A0}$$

$$D=5$$

$$a=0.007$$

$$T_0=450$$

$$T_s=300$$

$$d_h=-20000$$

$$f_{A0}=5$$

$$c_{pA}=40$$

$$k=\exp(3776.76*(1/450-1/T))$$

$$ca_0=0.25$$

$$ca=ca_0*((1-x)/(1+x))*(T/450)^y$$

$$r_A=k*ca$$

$$w_0 = 0, \quad w_f = 50$$

Initial value

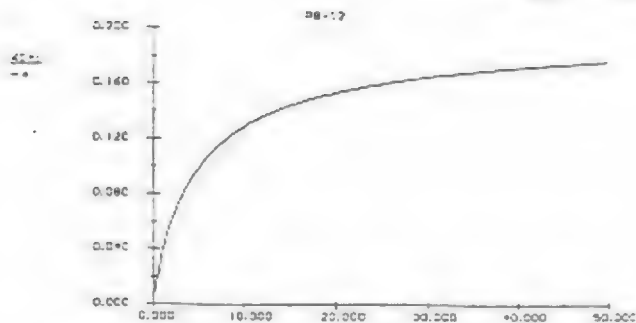
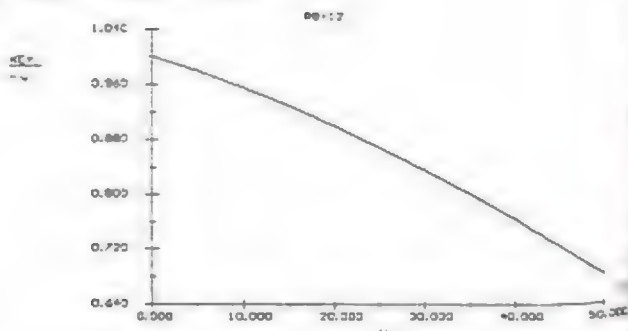
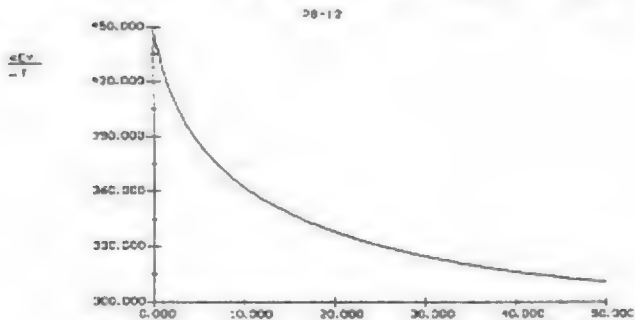
1

450

0

P8-12 (cont'd)

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	50	0	50
y	1	1	0.682386	0.682386
T	450	450	310.691	310.691
x	0	0.175758	0	0.175758
U	5	5	5	5
a	0.007	0.007	0.007	0.007
To	450	450	450	450
Ta	300	300	300	300
dh	-20000	-20000	-20000	-20000
fao	5	5	5	5
cpa	40	40	40	40
k	1	1	0.0232094	0.0232094
cao	0.25	0.25	0.25	0.25
ca	0.25	0.25	0.0825702	0.0825702
ra	-0.25	-0.0019164	-0.25	-0.0019164



P8-12

- (b) From the POLYMATH summary table it is apparent that the maximum value for $-r_A$ occurs at the beginning of the reactor.
- (c) The maximum value for the temperature also occurs at the beginning of the reaction.
- d) Doubling the heat-transfer coefficient causes a decrease in both the temperature, conversion and the pressure drop. Halving the heat-transfer coefficient cause an increase in temperature, conversion and pressure drop.

P8-13

$$K_C = \frac{C_C C_D}{C_A C_B} = \frac{X_e^2}{(1-X_e)^2}$$

$$\sqrt{K_C} = \frac{X_e}{1-X_e} \quad \text{or} \quad X_e = \frac{\sqrt{K_C}}{1 + \sqrt{K_C}}$$

POLYMATH

$$f(X_e) = X_e - (1-X_e) \sqrt{K_C}$$

$$K_C = 500,000 \exp \left[\frac{-30,000}{1.987} \left(\frac{1}{323} - \frac{1}{T} \right) \right]$$

T	X_e	T	X_e
300	1.000	440	0.585
320	0.999	460	0.40
340	0.995	480	0.26
360	0.984	500	0.1529
380	0.895	520	0.091
400	0.887	540	0.057
420	0.76	560	0.035

P8-13 cont'd

$$T = T_0 - \frac{\Delta H_R X}{C_{P_A} + C_{P_B}} = 300 - \frac{(-30,000)}{(25 + 25)} X = 300 + \frac{30,000}{50} X$$

$$T = 300 + 600 X$$

$$X = \frac{T - 300}{600}$$

*

The equations:

$$f(x) = x - (1-x) * k * .5$$

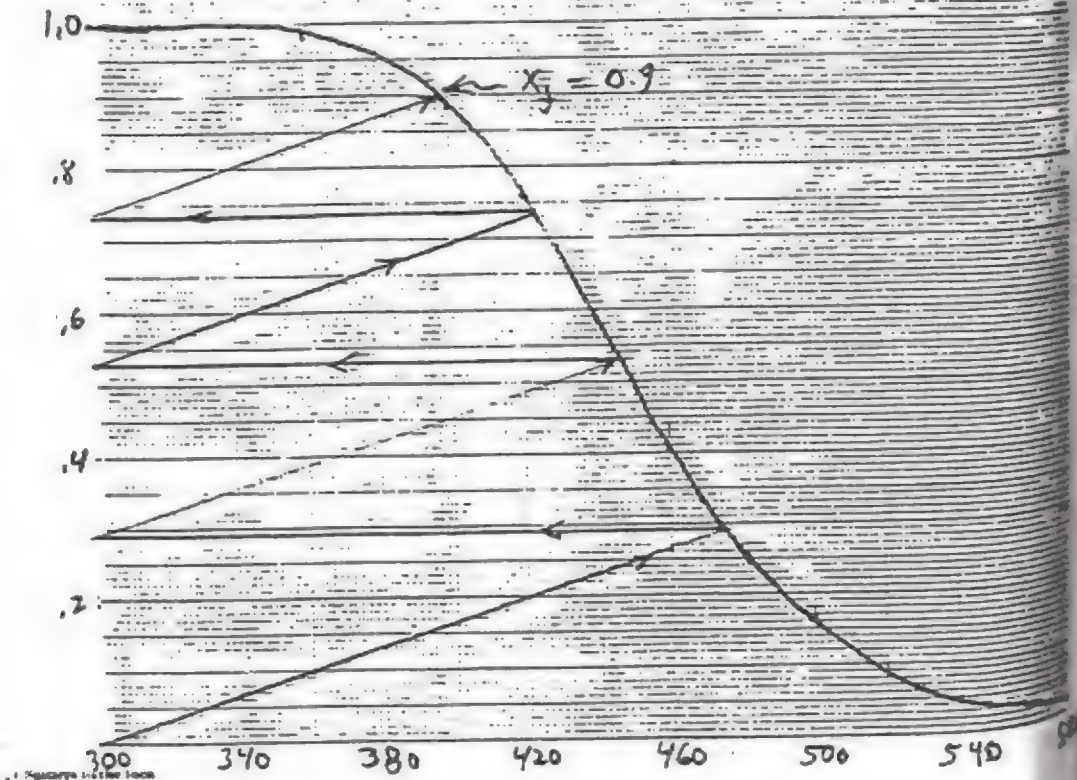
$$k = 500000$$

$$t = 390$$

$$e = \exp(-300000 * (1/323 - 1/t))$$

$$k = k * e$$

Search range: $x_{min} = 0.0$, $x_{max} = 1.0000$



P8-14 For first reactor

$$K_C = \frac{X_{e1}}{1-X_{e1}} \text{ or } X_{e1} = \frac{K_C}{1+K_C}$$

For 2nd reactor

$$K_C = \frac{\theta_{B2} + X_{e2}}{1-X_{e2}} \text{ or } X_{e2} = \frac{K_C - \theta_{B2}}{1+K_C}$$

For 3rd reactor

$$K_C = \frac{\theta_{B3} + X_{e3}}{1-X_{e3}} \text{ or } X_{e3} = \frac{K_C - \theta_{B3}}{1+K_C}$$

1st reactor: in first reactor $X_e = 0.2$

$$\text{Therefore } F_B = F_{A01}(.2)$$

2nd reactor: moles of A entering the 2nd reactor: $F_{A02} = 2F_{A01} - F_{A01}(.2) = 1.8 F_{A01}$

$$\theta_{B2} = \frac{.2F_{A01}}{1.8F_{A01}} = 0.11$$

$$-F_{A02} \sum C_p \theta_i (T-T_o) + F_{A02} X (-\Delta H_R) = 0$$

$$X = \frac{(C_{pA} + \theta_B C_{pB})(T-T_o)}{-\Delta H_R}$$

Slope is now negative

3rd reactor

$$\text{Say } X_{e2} = 0.3$$

$$\theta_B = (0.2F_{A01}) + .3F_{A02} = F_{A01}(.2 + (.3)(1.8))$$

$$F_{A03} = F_{A01} + F_{A02}(1-X_{e2}) = F_{A01} + 1.8F_{A01}(1-X_{e2}) = 1 + 1.8(1-.3)F_{A01}$$

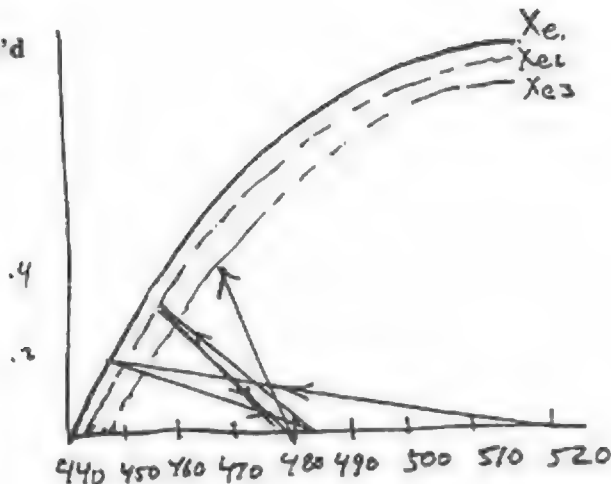
$$F_{A03} = 2.26 F_{A01}$$

B. Feed to reactor 3

$$F_{B3} = 2F_{A01} + .3F_{A02} = (.2 + (.3)(1.8)) F_{A01} = .07F_{A01}$$

$$\theta_{B3} = \frac{0.74}{2.26}$$

P8-14 cont'd



Feed temperature to reactor 2 is $\frac{520 + 450}{2} = 485$

Feed temperature to reactor 3 is $\frac{2 \cdot 460 + 520}{3} = 480$

$X_{\text{final}} = (.4)$

Moles of B = $(.2F_{A01}) + .3F_{A02} + .4F_{A03} = F_{A01} (.2 + .54 + (.4)(2.26)) = 1.64 F_{A01}$

$$X = \frac{F_B}{3F_{A01}} = 0.54$$

P8-15 The elementary, reversible, gas phase reaction $A + B \rightleftharpoons 2C$

Feed: $F_{A0} = F_{B0} = 20 \text{ mol/s} = 1200 \text{ mol/min.}$

$$P_0 = 580.5 \text{ kPa} = 5.74 \text{ atm.}$$

$$T_0 = 77^\circ\text{C} = 350^\circ\text{K}$$

$$Y_{A0} = Y_{B0} = 0.5$$

$$C_{A0} = \frac{Y_{A0} P_0}{RT_0} = \frac{(0.5)(5.74 \text{ atm.})}{\left(0.082 \frac{\text{L atm}}{\text{g mol}^\circ\text{K}}\right)(350^\circ\text{K})} = 0.1 \text{ g mol/L}$$

P8-15 cont'd

$$\text{Rate constant: } k = k_1 \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right]$$

$$= 0.035 \exp \left[\frac{70,000}{8.314} \left(\frac{1}{273} - \frac{1}{T} \right) \right]$$

$$= 0.035 \exp \left[8419.5 \left(\frac{1}{273} - \frac{1}{T} \right) \right]$$

(1)

Equilibrium constant

$$\Delta H_R (T_R) = 2H_C - H_A - H_B = 2(-45,000) + 40,000 + 30,000 = -20,000 \text{ J/mole}$$

$$\Delta C_p = 2C_{pC} - C_{pA} - C_{pB} = 2(20) - 25 - 15 = 0$$

$$\text{So } \Delta H_R (T) = \text{constant} = -20,000 \text{ J/mole}$$

(2)

$$K_C = K_{C1} \exp \left[\frac{\Delta H_R}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right]$$

$$\therefore K_C = 25,000 \exp \left[\frac{-20,000}{8.314} \left(\frac{1}{298} - \frac{1}{T} \right) \right]$$

$$K_C = 25,000 \exp \left[-2405.6 \left(\frac{1}{298} - \frac{1}{T} \right) \right]$$

(3)

k and K_C can be calculated by equation (1) and (3) if T is given.

$$K_C = \frac{C_C^2}{C_A C_B}$$

$$C_A = C_{A0}(1 - X) f$$

$$C_B = C_{A0}(1 - X) f \quad \text{where } f = \frac{T_0}{T}$$

$$C_C = 2C_{A0} X f$$

P8-15 cont'd

Substitute C_A , C_B , and C_C into K_C

$$K_C = \frac{4C_{A0}^2 X^2 f^2}{C_{A0}^2 (1-X)^2 f^2} = \frac{4X^2}{(1-X)^2} \quad (4)$$

$$\therefore \sqrt{K_C} = \frac{2X}{1-X} \quad \text{or} \quad X_{eq} = \frac{\sqrt{K_C}}{2 + \sqrt{K_C}} \quad (5)$$

Calculate $\sqrt{K_C}$ as a function of temperature from equation (3), substitute in equation (5) to get X_{eq} as a function of T . Energy balance for adiabatic condition:

$$-X \Delta H_R = \sum \theta_i C_{pi} (T - T_0) \quad (6)$$

$$\theta_A = \theta_B = 1, \theta_C = 0, T_0 = 350K$$

$$\text{Substitute: } +20,000X = (25 + 15)(T - 350) \Rightarrow T = 500X + 350$$

$$\text{or } X = 0.002(T - 350) \quad (7)$$

Equations (3) = (4):

$$\frac{4X^2}{(1-X)^2} = 25000 \exp \left[-2405.6 \left(\frac{1}{298} - \frac{1}{350 + 500X} \right) \right]$$

$$X_{eq} = 0.8667$$

$$0.85X_{eq} = 0.7366 \approx 0.7$$

(a) Plug flow reactor design equation:

$$V = F_{A0} \int \frac{dX}{-r_A} \quad (8)$$

$$\text{Rate law: } -r_A = k \left[C_A C_B \cdot \frac{C_C^2}{K_C} \right]$$

$$-r_A = k C_{A0}^2 f^2 \left[(1-X)^2 \cdot \frac{(2X)^2}{K_C} \right] \quad (9)$$

$$\text{So } V = \frac{F_{A0}}{C_{A0}^2} \int_0^{0.7} \frac{dX}{kf^2 \left[(1-X)^2 \cdot \frac{4X^2}{K_C} \right]} = \frac{1200}{(0.1)^2} \int_0^{0.7} f(X) dX$$

$$V = 1.2 \times 10^5 \int_0^{0.7} f(X) dX \quad \text{where } f(X) = \frac{1}{kf^2 \left[(1-X)^2 \cdot \frac{4X^2}{K_C} \right]} \quad (10)$$

To evaluate the integral, we need to evaluate $f(X)$ as a function of X . This is done in the table below:

X	$T^{\circ}\text{K}$ (eqn. 7)	K_C (eqn. 3)	k (eqn. 1)	$f(X)$ (eqn. 9)
0	350	7534.8	30.96	0.0323
0.1	400	3191.1	626.1	2.58×10^{-3}
0.2	450	1635.9	6491.5	3.98×10^{-4}
0.3	500	958.5	4.216×10^4	9.89×10^{-5}
0.4	550	618.9	1.949×10^5	3.53×10^{-5}
0.5	600	429.9	6.978×10^5	1.70×10^{-5}
0.6	650	315.8	2.054×10^6	1.08×10^{-5}
0.7	700	192.8	1.155×10^7	4.98×10^{-6}

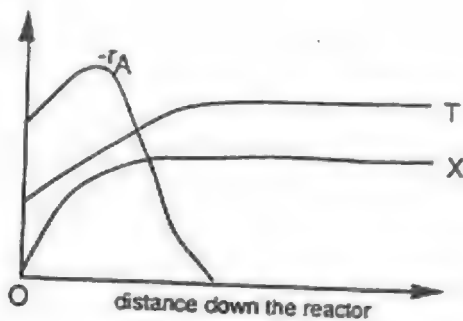
The integral can be evaluated using Simpson's rule for the first six segments and trapezoidal rule for the last segment.

$$I = \int_0^{0.7} f(X) dX \cong \frac{0.1}{3} [0.0323 + 4(2.58 \times 10^{-3}) + 2(3.98 \times 10^{-4}) + 4(9.89 \times 10^{-5}) + 2(3.53 \times 10^{-5}) + 4(1.70 \times 10^{-5}) + 1.08 \times 10^{-5}] + \frac{0.1}{2} [1.08 \times 10^{-5} + 4.98 \times 10^{-6}]$$

$$I = 1.5 \times 10^{-3}$$

$$V_{PFR} = (1.2 \times 10^5)(1.5 \times 10^{-3}) = 180 \text{ L}$$

(b) Exothermic, adiabatic



(c) CSTR design equation: $V = \frac{F_{A0} X_A}{-r_A}$

$$V = \frac{F_{A0} X}{k C_{A0}^2 f^2 \left[(1-X)^2 - \frac{4X^2}{K_C} \right]}$$

P8-15 cont'd

$$\frac{X}{k f^2 \left[(1-X)^2 - \frac{4X^2}{K_C} \right]} = \frac{1500L \times (0.1)^2 \left(\frac{\text{mol}}{l} \right)^2}{1200 \frac{\text{mol}}{\text{min}}} = 0.0125$$

$$(1-X)^2 - \frac{4X^2}{K_C} = 80 \frac{X}{f^2 k}$$

$$1-2X+X^2 - \frac{4X^2}{K_C} = \frac{80X}{f^2 k}$$

$$\left(1 - \frac{4}{K_C} \right) X^2 - \left(2 + \frac{80}{f^2 k} \right) X + 1 = 0$$

$$\text{Let } b_1 = 1 - \frac{4}{K_C} \text{ and } b_2 = 2 + \frac{80}{f^2 k} \quad (11)$$

$$\Rightarrow X = \frac{b_2 \pm \sqrt{b_2^2 - 4b_1}}{2b_1} \quad (12)$$

Nonadiabatic energy balance:

$$\frac{-U A}{F_{A0}} (T - T_A) - X \Delta H_R = \sum \theta_i C_{pi} (T - T_0)$$

$$\frac{-10 \frac{\text{W}}{\text{m}^2 \text{K}} \times 2}{1200 \frac{\text{mol}}{\text{min}}} \times \frac{1 \text{kW}}{1000 \text{W}} \times \frac{1 \text{hr}}{60 \text{min}} \times \frac{3.6 \times 10^6 \text{ J}}{1 \text{KW} \cdot \text{hr}} (T - 290) + 20000X = 40(T - 350)$$

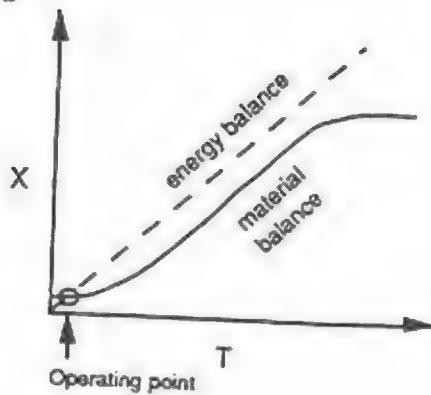
$$-T + 290 + 20,000X = 40T - 14,000$$

$$T = 348.5 + 487.8 X \quad (13)$$

So the procedure to calculate X is as follows:

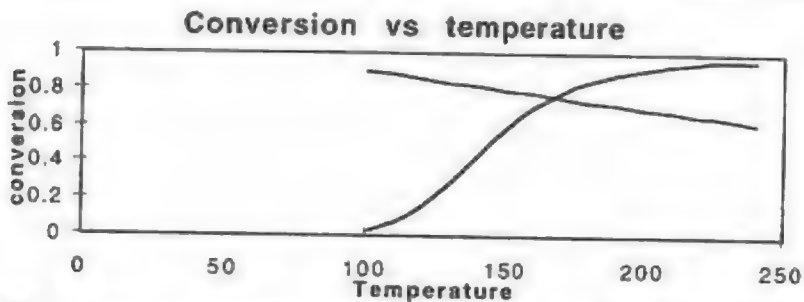
1. Choose increments in T and calculate X as a function of T from equation (13). This is the value given by energy balance.
2. Choose increments in T and calculate b₁ and b₂ from equation (11). (K_C and k can be calculated from equation (3) and c1) respectively.)
3. Calculate X, discarding X > 1 or X < 0. This is the value of X given by material balance.
4. Plot X vs. T given by equation (13) and (11) on the same graph. The intersection gives the conversion in the reactor. A typical graph looks like the following:

P8-15 cont'd



The actual calculation gives: $X = 0$ which is the conversion in CSTR.

d) The same equations can be used except that $\Delta H_r = 20000$ and $T_0 = 550K$. The following graph shows the equilibrium conversion for this case.



The following POLYMATH program gives the PFR volume necessary to get a conversion of .65.

Equations:

```
d(x)/d(v) = -ra/fao
fao = 1200
T = 500 * x + 550
cao = .064
To = 550
k = .035 * exp(8419.5 * (1/273 - 1/T))
Kc = 25000 * exp(2405.6 * (1/298 - 1/T))
f = To/T
```

```
ca = cao * (1 - x) * f
cb = cao * (1 - x) * f
cc = 2 * cao * x * f
ra = -k * (ca * cb - cc^2 / Kc)
v0 = 0, v1 = 1e-08
```

Initial value
0

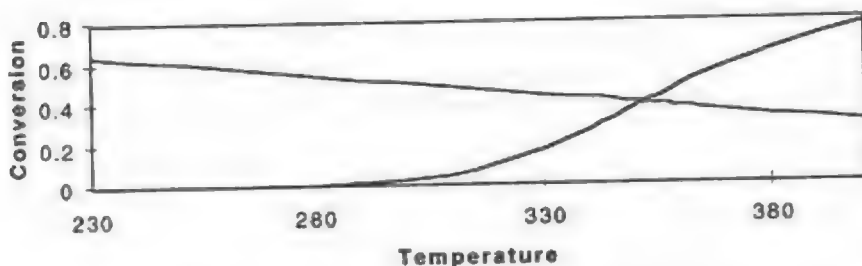
Variable

Variable	Initial value	Maximum value	Minimum value	Final value
v	0	1e-08	0	1e-08
x	0	0.649546	0	0.649546
fao	1200	1200	1200	1200
T	550	550	225.227	225.227
cao	0.064	0.064	0.064	0.064
To	550	550	550	550
k	194867	194867	5.04735e-05	5.04735e-05
Kc	1.00983e+06	1.00983e+06	1841.48	1841.48
f	1	2.44198	1	2.44198
ca	0.064	0.064	0.0547713	0.0547713
cb	0.064	0.064	0.0547713	0.0547713
cc	0	0.203031	0	0.203031
ra	-798.173	-1.50285e-07	-798.173	-1.50285e-07

P8-15 cont'd

The CSTR conversion can be found similarly to the equilibrium conversion. The following graph was made to find the conversion.

Conversion vs temperature



The graph shows a conversion of .39 at a temperature of 351.8K

e) If the reaction is left in a large enough volume it will "runaway". If any of the quantities get bigger, then it will run away even faster.

f) The ambient temperature around the CSTR has little effect on the conversion in the CSTR.

P8-16

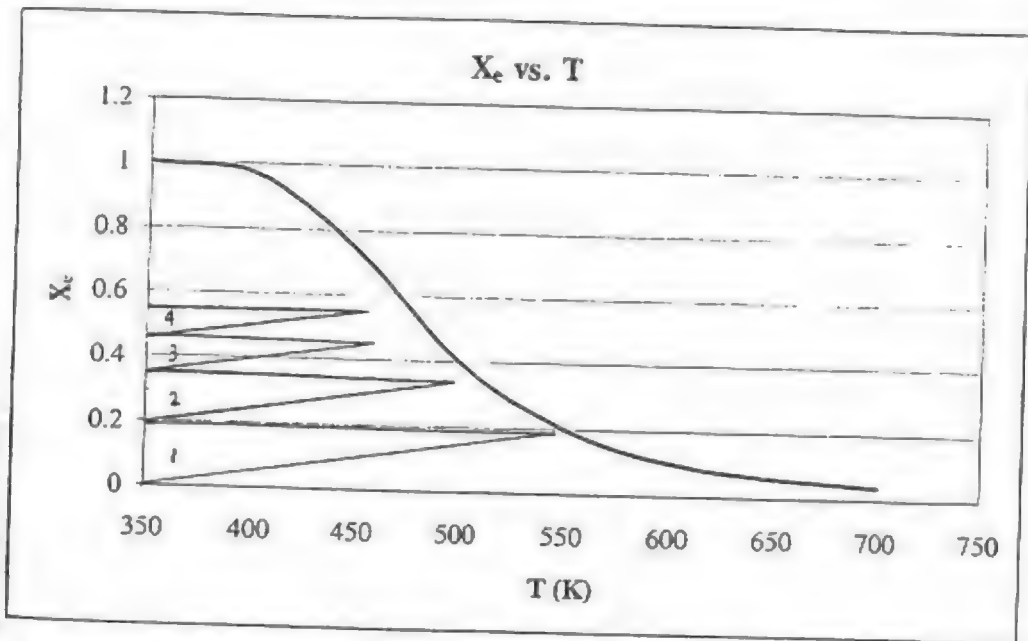
First, we must determine a relationship between the change in T and the change in X.

$$\text{Energy Balance: } \frac{dT}{dW} = \frac{UA(T_s - T) + (-r_A)(-\Delta H_R)}{F_{A0}[C_{pA} + \Theta_B C_{pB} + X\Delta\Delta_p]} = \frac{(-r_A)(-\Delta H_R)}{F_{A0}[C_{pA} + C_{pB}]}$$

$$\text{Mole Balance: } \frac{dX}{dW} = \frac{-r_A}{F_{A0}}$$

$$\begin{aligned} \text{Combine: } \frac{\frac{dT}{dW}}{\frac{dX}{dW}} &= \frac{dT}{dX} = \frac{-\Delta H_R}{C_{pA} + \Theta_B C_{pB} + \Theta_i C_{pi}} = \frac{10,000}{2 + 5 + 2(1.5)} = 1,000 \\ \frac{dT}{dX} &= 1,000 \end{aligned}$$

After determining this relationship, graph the data given in the problem statement as X_c vs. T. From this graph we can determine the number of reactors required to achieve any exit conversion.



From this it can be seen that it would require 4 reactors in series to achieve 55% (>50%) overall conversion. To achieve 95% conversion would require large numbers of reactors in series. This would be of concern because with each reactor the change in pressure increases, which can cause instability.

P8-17

(a)

$$G(T) = \Delta H_R X$$

$$X = \frac{\tau k}{1 + \tau k} \quad k = 6.6 \times 10^3 \exp \left[\frac{E}{R} \left(\frac{1}{350} - \frac{1}{T} \right) \right]$$

$$R(T) = C_{p0} (1 + \kappa)(T - T_c)$$

$$C_{p0} = \sum \Theta_i C_{pi} = \Theta_A C_{pA} + \Theta_I C_{pI} = 20 + 30 = 50$$

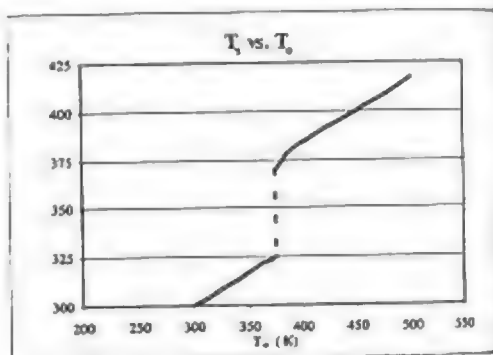
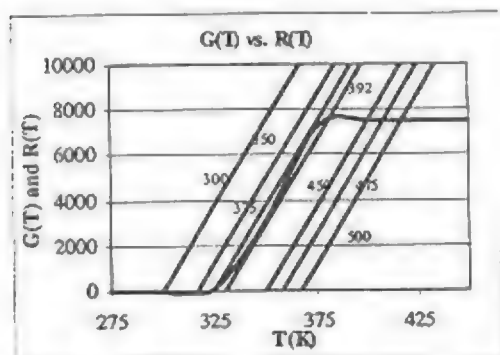
$$\kappa = \frac{UA}{C_{p0} F_{A0}} = \frac{8000}{(50)(80)} = 2$$

$$T_c = \frac{T_0 F_{A0} C_{p0} + UA T_s}{UA + C_{p0} F_{A0}} = \frac{\kappa T_s + T_0}{1 + \kappa} = \frac{(2)(300) + 450}{1 + 2} = 350$$

To find the steady-state T, we must set $G(T) = R(T)$. This can be done either graphically or using the solver in Excel. We find that for $T_0 = 450$ K, the steady-state temperature is 358 K.

(b)

First, we must plot $G(T)$ and $R(T)$ for many different T_0 's on the same plot. From this we generate data that we use to plot T_i vs. T_0 .



- (c) For high conversion the feed stream must be preheated to at least 390 K (117°C). At this temperature, $X = 0.98$ and $T = 380$ K (107°C) in the CSTR. Any feed temperature above this point will provide higher conversions.
- (d) For a temperature of 375 K, the conversion is 0.968.
- (e) The inlet extinction temperature is 375 K (102°C).

P8-18

a) P8-6 is adiabatic so the radial reactor has no effect on it.

(b)

$$\frac{dX}{dW} = \frac{-r_A}{F_{A0}}$$

$$-r_A = kC_A$$

$$C_A = C_{A0} \frac{1 - X}{1 + X} \frac{T_0}{T} y$$

$$\frac{dy}{dW} = \frac{-\alpha}{2y}$$

$$\frac{dT}{dW} = \frac{U(r) \frac{2h}{\rho} (T_A - T) + (-r_A)(-\Delta H_R)}{F_{A0} C_{pA}}$$

$$U = U(r_0) \left(\frac{r_0}{r} \right)^5 \left(\frac{T}{T_0} \right)^5$$

Since h and p are unknown, we will assume that they are both equal to one. We will also assume that r varies as W^5 varies.

so:

$$\frac{dT}{dW} = \frac{U(r)(T_A - T) + (-r_A)(-\Delta H_R)}{F_{A0} C_{pA}}$$

$$U = U(r_0) \left(\frac{W_0^5}{W} \right)^5 \left(\frac{T}{T_0} \right)^5$$

Plugging those into POLYMATH gets the following graph.

Equations:

$$d(y)/d(w) = -\alpha p / (2 \cdot y)$$

$$d(x)/d(w) = -r_A / f_{A0}$$

$$d(T)/d(w) = (U \cdot (T_A - T) + (-r_A) \cdot (-\Delta H_R)) / (f_{A0} \cdot 40)$$

$$f_{A0} = 5$$

$$\alpha p = .007$$

$$T_A = 300$$

$$\Delta H_R = -20000$$

$$w_0 = .01$$

$$T_0 = 450$$

$$a = 31400$$

$$R = 8.413$$

$$c_{A0} = 9.22 / (.082 \cdot 450)$$

$$x_1 = 1000 \cdot x$$

$$y_1 = 1000 \cdot y$$

$$U = 5 \cdot (w_0^5 / w^5) \cdot .5 \cdot (T / T_0)^5 \cdot y_1^5 \cdot (1 - x)^{.5}$$

$$k = \exp(e / R \cdot (1 / 450 - 1 / T))$$

$$c_A = c_{A0} \cdot (1 - x) \cdot T_0 / T$$

$$cc = 2 \cdot x \cdot c_{A0} \cdot T_0 / T$$

$$K_c = 25000 \cdot \exp(\Delta H_R / R \cdot (1 / 298 - 1 / T))$$

$$cb = c_A$$

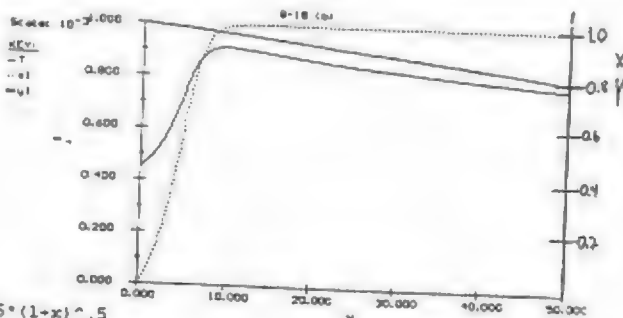
$$f_A = k \cdot (c_A \cdot cb - cc^2 / K_c)$$

Initial value

1

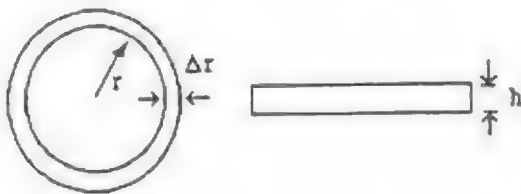
0

450



Variable	Initial value	Maximum value	Minimum value	Final value
w	0.01	50	0.01	50
y	1	1	0.806269	0.806269
x	0	1	0	1
T	450	908.557	450	775.479
fA0	5	5	5	5
alp	0.007	0.007	0.007	0.007
TA	300	300	300	300
Dhr1	-20000	-20000	-20000	-20000
w0	0.01	0.01	0.01	0.01
T0	450	450	450	450
a	31400	31400	31400	31400
R	8.413	8.413	8.413	8.413
cA0	0.249854	0.249854	0.249854	0.249854
x1	0	1000	0	1000
y1	1000	1000	806.269	806.269
U	5	5	0.991839	0.991839
ca	1	0.1	0.021683	0.021683
cc	0	0.144234	0	0.144234
Kc	7530.55	7530.55	4276.15	4276.15
cb	0.1	0.1	0.021683	0.021683
fA	-0.110572	-0.0440483	-1.28948	-0.0440483

(c)



$$W = \rho V = \rho \pi r^2 h \Rightarrow dW = 2\pi r h dr$$

$$\text{Material balance: } F_A|_r - F_A|_{r+\Delta r} + r_A \Delta W = 0$$

$$F_A|_r - F_A|_{r+\Delta r} + 2\pi r h (r_A) \Delta r = 0$$

Taking the limit as $\Delta r \rightarrow 0$

$$\frac{dF_A}{dr} = (r_A) 2\pi r h$$

$$F_A = F_{AO} (1 - X_A) = \frac{dF_A}{dr} = -F_{AO} \frac{dX_A}{dr}$$

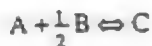
$$\text{so: } \frac{dX_A}{dr} = \frac{-2\pi r h \rho (r_A)}{F_{AO}} \quad (1)$$

$$\text{or: } \frac{dX_A}{dW} = -\frac{r_A}{F_{AO}} \quad (2)$$

Assuming pressure drop is negligible. The rate equation is:

$$-r_A = k \left(\frac{P_{SO_2}}{P_{SO_3}} \right)^{1/2} \left[P_{O_2} - \left(\frac{P_{SO_2}}{K_P P_{SO_2}} \right)^2 \right]$$

The stoichiometry: $SO_2 + \frac{1}{2} O_2 \rightleftharpoons SO_3$



$$\delta = -0.5, y_{AO} = 0.11 \therefore \epsilon = y_{AO} \delta = -0.055 ; \theta_C = 0 ; \theta_B = \frac{10}{11} = 0.91$$

$$P_{SO_2} = P_{SO_{20}} \frac{1 - X_A}{1 + \epsilon X_A} ; P_{SO_3} = P_{SO_{20}} \frac{X_A}{1 + \epsilon X_A} ; P_{O_2} = P_{SO_{20}} \frac{(0.91 - 0.5X_A)}{1 + \epsilon X_A}$$

$$\text{Then: } -r_A = k(t) \left(\frac{1 - X_A}{X_A} \right)^{1/2} \left[P_{SO_{20}} \left(\frac{0.91 - 0.5X_A}{1 - 0.055X_A} \right) - \frac{X_A^2}{(1 - X_A)^2 K_P^2} \right] \quad (3)$$

Equation (3) is true for $X_A < 0.05$ for $X_A \geq 0.05$

$$-r_A = k(t) (4.35) \left[0.22 \left(\frac{0.91 - 0.025}{1 - 0.055(0.05)} \right) - \frac{0.0025}{(1 - 0.05)^2 K_p^2} \right]$$

$$-r_A = k(t) \left[0.848 - \frac{0.01205}{K_p^2} \right] \quad (4)$$

Energy balance:

$$F_{AO} (\Sigma \theta_i C_{pi} + X \Delta C_p) T_{lr} - F_{AO} (\Sigma \theta_i C_{pi} + \Delta C_p X) T_{lr+\Delta r} + r_A \Delta W (\Delta H_R) - (2) (\Delta A) U(r) (T - T_A) = 0$$

$$\text{or: } F_{AO} (\Sigma \theta_i C_{pi} + X \Delta C_p) T_{lr} - F_{AO} (\Sigma \theta_i C_{pi} + \Delta C_p X) T_{lr+\Delta r} + r_A 2\pi r h_p (\Delta H_R) \Delta r - (2) (2\pi r \Delta r) U(r) (T - T_A) = 0$$

Taking the limit as $\Delta r \rightarrow 0$:

$$F_{AO} (\Sigma \theta_i C_{pi} + X \Delta C_p) \frac{dT}{dr} = -U(r) 4\pi r (T - T_A) + (-r_A) (-\Delta H_R) 2\pi r h_p$$

Rearranging:

$$\frac{dT}{dr} = \frac{-U(r) 4\pi r (T - T_A) + (-r_A) (-\Delta H_R) 2\pi r h_p}{F_{AO} (\Sigma \theta_i C_{pi} + X \Delta C_p)} \quad (5)$$

$$\text{or: } \frac{dT}{dW} = \frac{-U(r) \frac{2h}{\rho} (T - T_A) + (-r_A) (-\Delta H_R)}{F_{AO} (\Sigma \theta_i C_{pi} + X \Delta C_p)} \quad (6)$$

$$\text{Assume that: } U(r) = U(r_o) \left(\frac{v}{v_o} \right)^{1/2} ; v = \frac{v_o r_o}{r} (1 + \epsilon X) \frac{T}{T_o}$$

$$\text{Therefore: } U(r) = U(r_o) \left(\frac{r_o}{r} \right)^{1/2} \left(\frac{T}{T_o} \right)^{1/2} (1 - 0.055 X_A)^{1/2}$$

From example 8-10, we have:

$$K_p = \exp \left[\frac{42,311}{RT} - 11.24 \right] (K_p \text{ in atm}^{-1/2}, T \text{ in } ^\circ R) \quad (7)$$

$$k = \exp \left[\frac{-176,008}{T} - 110.1 \ln T + 912.84 \right] \quad (8)$$

$$\Delta H_R(T) = -42,471 - (1.563)(T - 1260) + (1.36 \times 10^{-3}) \left(\frac{T^2 - 1260^2}{2} \right)$$

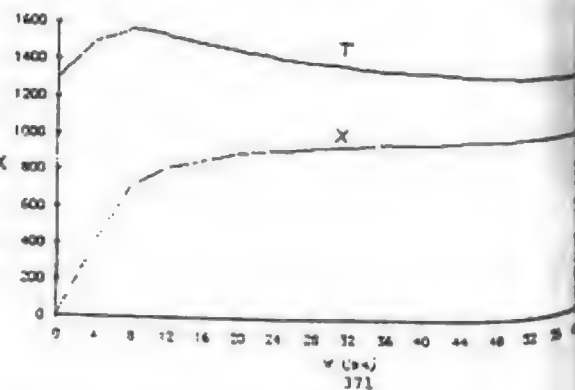
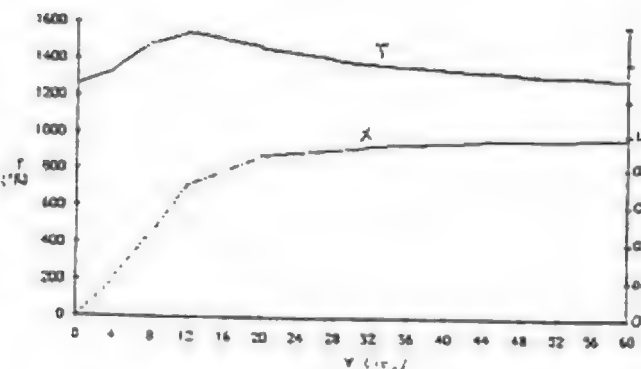
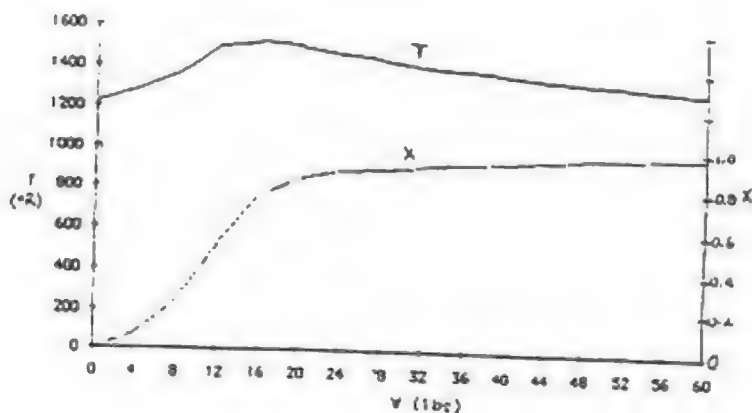
$$- (2.459 \times 10^{-7}) \left(\frac{T^3 - 1260^3}{3} \right) \text{ where } \Delta H_R \text{ in } \frac{\text{Btu}}{\text{lbmole}} \quad (9)$$

P8-18 (cont'd)

$$\sum \theta_i C_{p,i} = 57.23 + 0.014T - 1.788 \times 10^{-6} T^2$$

(10)

Since equations (1) to (10) must be solved together as two pairs of coupled differential equations, they must be solved on a computer, employing numerical methods such as Runge-Kutta. The results follow:



d)

$$\frac{dX}{dr} = \frac{-2\pi r h \rho (-r_A)}{F_{A0}}$$

$$-r_A = k \left(C_A C_B - \frac{C_C^2}{K_C} \right)$$

$$C_A = C_B = C_{A0}(1-X) \frac{T_0}{T}$$

$$C_c = 2C_{A0}X \frac{T_0}{T}$$

$$\frac{dT}{dr} = \frac{U(r)4\pi r(T_A - T) + (-r_s)(-\Delta H_{R1})}{F_{A0}(C_{pA} + C_{pB})}$$

$$U = U(r_0) \left(\frac{r_0}{r} \right)^5 \left(\frac{T}{T_0} \right)^5$$

Plug those into POLYMATH to generate this graph of temperature and conversion as a function of radius.

Equations:

$$d(x)/d(r) = -2 \cdot 3.1416 \cdot h \cdot (r_a) / f_{A0}$$

$$d(T)/d(r) = (U \cdot 4 \cdot 3.1416 \cdot r \cdot (T_A - T) + (-r_s) \cdot (-\Delta H_{R1})) / (f_{A0} \cdot (C_{pA} + C_{pB}))$$

pb1

Ta=173

Dhr1=-20000

fao=1200

cpa=25

cpb=15

h=5

ra=5

Ta=150

E=70000

Ra=31

case=1

Ta=31.3*(ra/r)^0.5*(T/To)^0.5

U=0.25*exp(E/R*(1/273-1/T))

Ca=Ca0*(1-x)/(1-x)*(To/T)^y

ra=-k*Ca

ky=0.02

Ta

Dhr1

fao

cpa

cpb

h=0.5

ra

To

E=70000

Ca0

U

Ca

ky

Wf=50

Wf=50

Wf=50

Wf=50

Wf=50

Wf=50

Wf=50

Wf=50

Wf=50

Wf=50

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Wf=50

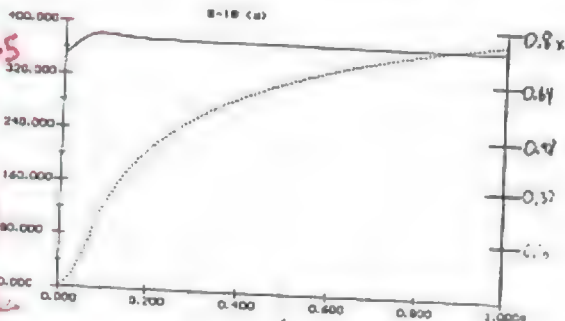
Wf=50

Wf=50

Wf=50

Wf=50

Variable	Initial value	Maximum value	Minimum value	Final value
r	0.5	1000		
x	0	0.768838	0.5	1000
T	150	381.135	350	0.768838
Ta	373	373	373	373.135
Dhr1	-20000	-20000	-20000	-20000
fao	1200	1200	1200	1200
cpa	25	25	25	25
cpb	15	15	15	15
h	0.5	0.5	0.5	0.5
ra	0.5	0.5	0.5	0.5
To	350	350	350	350
E	70000	70000	70000	70000
R	8.31	8.31	8.31	8.31
Ca0	0.1	0.1	0.1	0.1
U	33.3	33.3	0.768826	0.768826
k	31.0572	225.061	31.0572	138.135



P8-19

The energy balance for a CSTR:

$$-F_{A0}X\Delta H_{Rx}(T) = F_{A0}\left[\sum \theta_i \tilde{C}_{pi}(T - T_0) + \frac{UA}{F_{A0}}(T - T_a)\right]$$

$$F_{A0}X = -r_A V$$

C_{pS} is independent of temperature so:

$$C_{p0}(T - T_0) = C_{pS}$$

$$G(T) = (-\Delta H_{Rx})\left(\frac{-r_A V}{F_{A0}}\right)$$

$$R(T) = F_{A0}C_{pS} + UAT_r - UAT$$

So taking the derivative of those with respect to temperature we get:

$$\frac{dR(T)}{dT} = UA$$

$$\frac{dG(T)}{dT} = \frac{-\Delta H_{Rx}}{F_{A0}} \frac{d(-r_A)}{dT}$$

where

$$\frac{d(-r_A)}{dT} = \frac{E}{RT^2}(-r_A)$$

Set those two equations equal to each other and then divide the energy balance by the resulting equation and the following is found.

$$\ln \frac{1.421}{1.127} = \left[\frac{E}{R} \left(\frac{323 - 313}{323 * 313} \right) \right]$$

$$E = 19474$$

$$\frac{F_{A0}C_{pS}}{UA} + (T_r - T_a) > \frac{RT_r^2}{E} \quad \text{and it will be a runaway reaction.}$$

$$\frac{90000 \text{ g/min} * 4 \text{ J/g} * 1 \text{ min/60 s}}{120 \text{ J/s} * \text{m}^2 * \text{K} * \text{A}} + (358 - 273) > \frac{8.314 * 358^2}{19474}$$

$$6000 + 10200 > 6566 * A$$

$$A < 2.5 \text{ m}^2 \text{ for it to be a runaway.}$$

a) $A \xrightarrow{\quad} B$

$$\text{Mole balance: } V = \frac{F_{A0}x}{-r_A} = \frac{v_0 C_{A0}x}{k[C_A - C_B/K_e]}$$

$$\left(\frac{v}{v_0}\right)k[(1-x) - x/K_e]$$

$$x[1 + \tau k(1 + 1/K_e)] = \tau k$$

$$x = \frac{\tau k}{1 + \tau k(1 + 1/K_e)}$$

$$G(T) = (-\Delta H_{Rx})x = 80000 * x$$

$$k = 1 \text{ min}^{-1} \quad \tau = 10 \text{ min.} \quad K_e = 100$$

$$x = \frac{10}{1 + 10(1.01)} = .901$$

$$G(400) = 72080 \text{ cal/mol}$$

$$\text{b) } \kappa = \frac{UA}{F_{A0}C_{pA}} = \frac{3600}{10 * 40} = 9$$

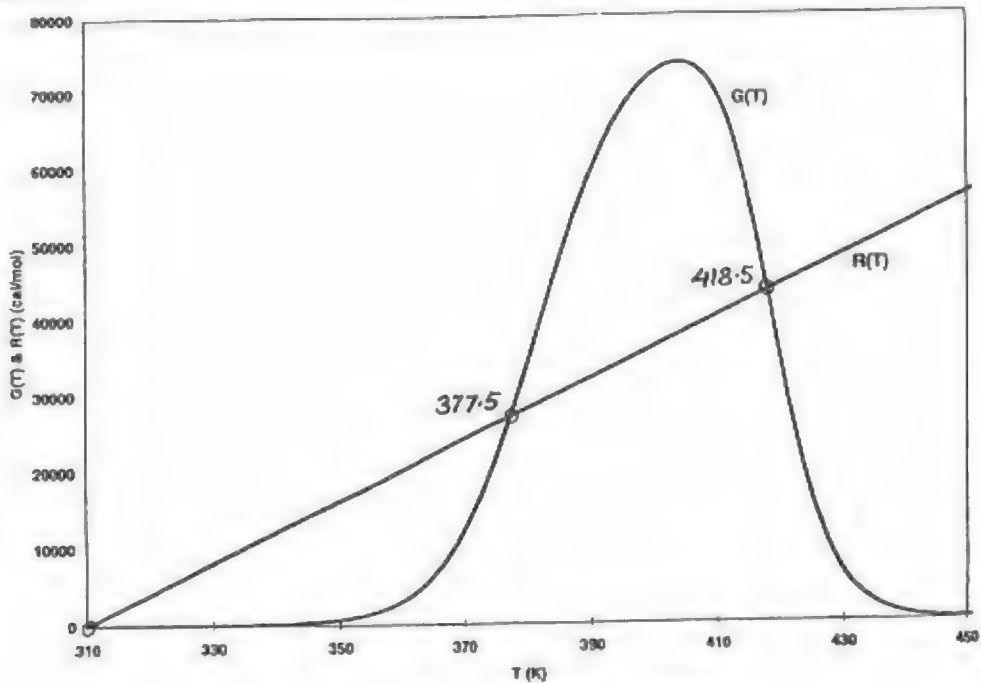
$$R(T) = C_{pA}(1 + \kappa)(T - T_c) = 400(T - T_c)$$

$$T_c = \frac{T_0 + \kappa T_a}{1 + \kappa} = \frac{310 + 9 * 310}{1 + 9} = 310$$

$$R(T) = 400(T - 310)$$

The following plot gives the steady state temperatures of 310, 377.5 and 418.5 K.

P8-20 cont'd



c) 310K and 418.5 K are locally stable steady-state points.

d)

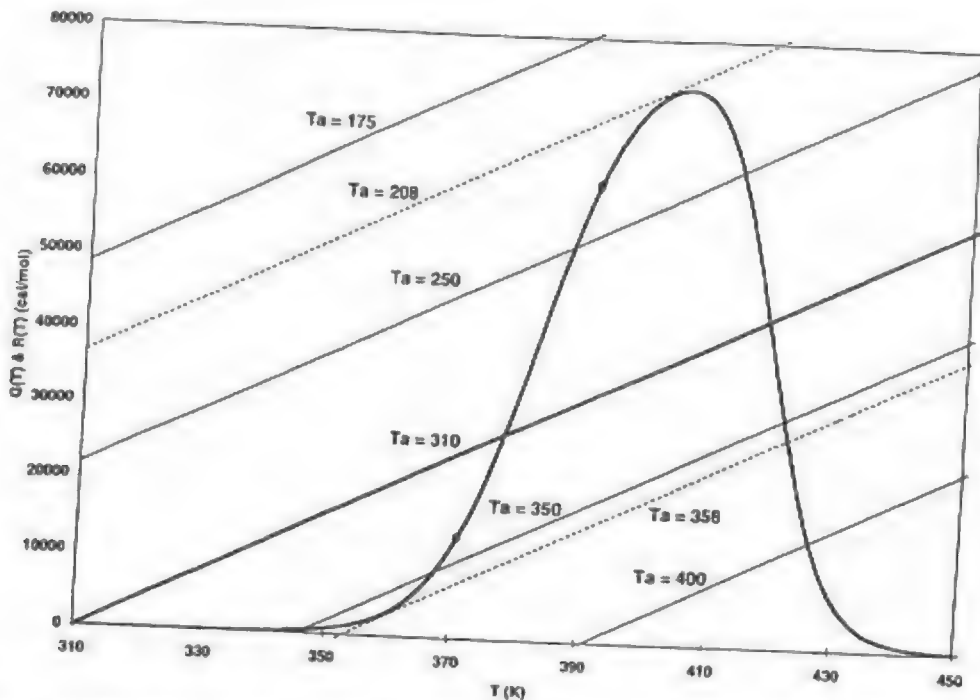
$$R(418.5) = 400(418.5 - 310) = 43400$$

$$G(418.5) = 43400 = 80000 \cdot x$$

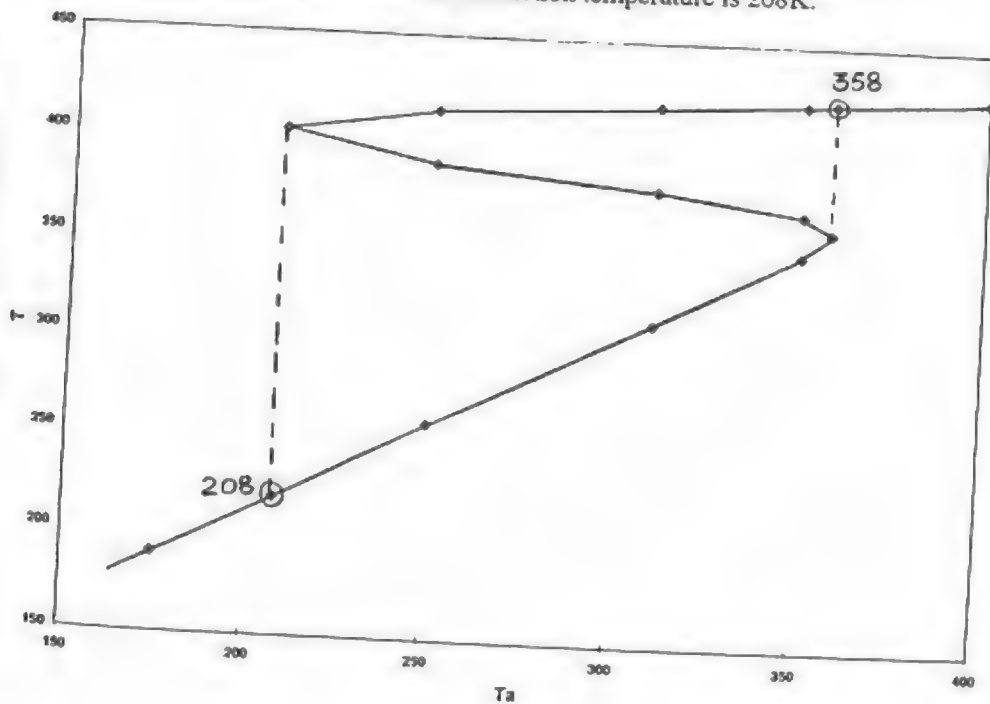
$$x = \frac{43400}{80000} = .54$$

e) This plot shows T_s varied.

P8-20 cont'd

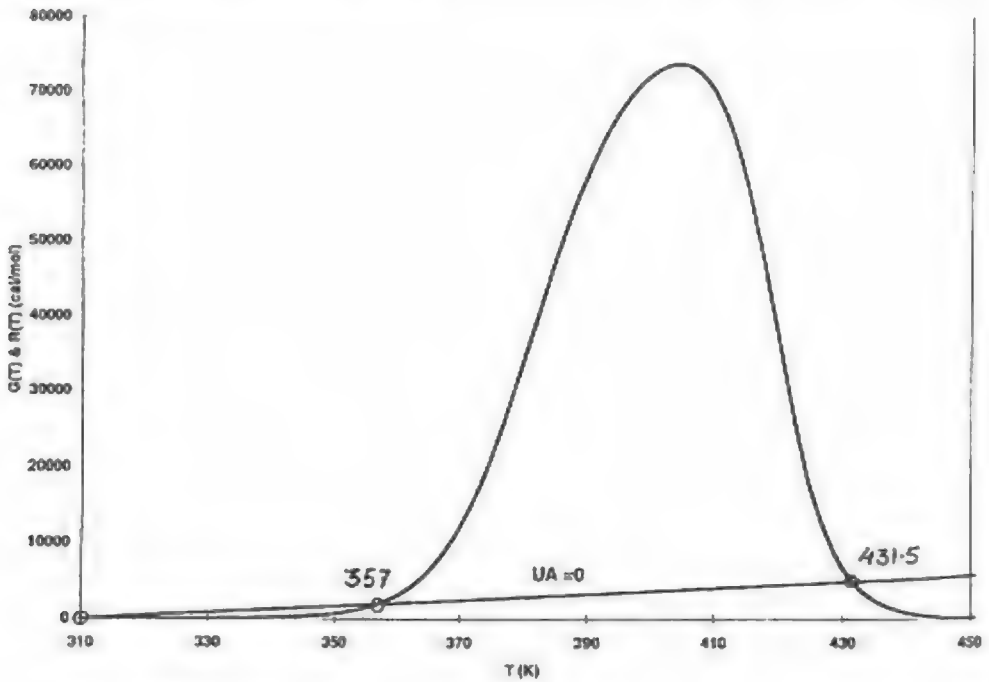


This plot shows the way to find the ignition and extinction temperatures. The ignition temperature is 358 K. The extinction temperature is 208 K.



P8-20 cont'd

f) This plot shows what happens if the heat exchanger quits. The upper steady-state temperature now becomes 431.5 K.



g) No solution will be given.

8-21 Given the first order, irreversible, liquid phase reaction:
 $A \rightarrow B$

Jacketed CSTR $UA = 1.0 \text{ cal/min. } ^\circ\text{C}$
 $T_A = 100^\circ\text{C}$

Pure A feed: $F_{A0} = 0.5 \text{ g mole/min}$; $C_{pA} = C_{pB} = 2 \frac{\text{cal}}{\text{g mole } ^\circ\text{C}}$; $\Delta C_p = C_{pB} - C_{pA} = 0$

$$\Delta H_R = -200 \frac{\text{cal}}{\text{g mole A}} = \text{constant}$$

Design equation: $V = \frac{F_{A0} X}{-r_A}$

Rate Law: $-r_A = k C_A$

Stoichiometry: $C_A = C_{A0} (1 - X)$

Energy balance: $-UA(T - T_A) - F_{A0} X (\Delta H_R) = F_{A0} \sum \theta_i C_{pi} (T - T_0)$

$$V = \frac{F_{A0} X}{-r_A} = \frac{F_{A0} X}{k C_{A0} (1 - X)} = \frac{v_0}{k (1 - X)} \quad (1)$$

Simplification of equation (1) with $\tau = \frac{V}{v_0}$ gives

$$X = \frac{\tau k}{1 + \tau k} = \frac{1}{1 + \frac{1}{\tau k}} \quad (2)$$

The equation for heat generation curve is:

$$Q_g = F_{A0} X (-\Delta H_R) = \frac{F_{A0} (-\Delta H_R)}{1 + \frac{1}{\tau k}} \quad (3)$$

This is the curve plotted in the problem statement. From equation (3) we can get:

$$X = \frac{Q_g}{F_{A0} (-\Delta H_R)} = \frac{Q_g}{(0.5)(200)} = \frac{Q_g}{100} \quad (4)$$

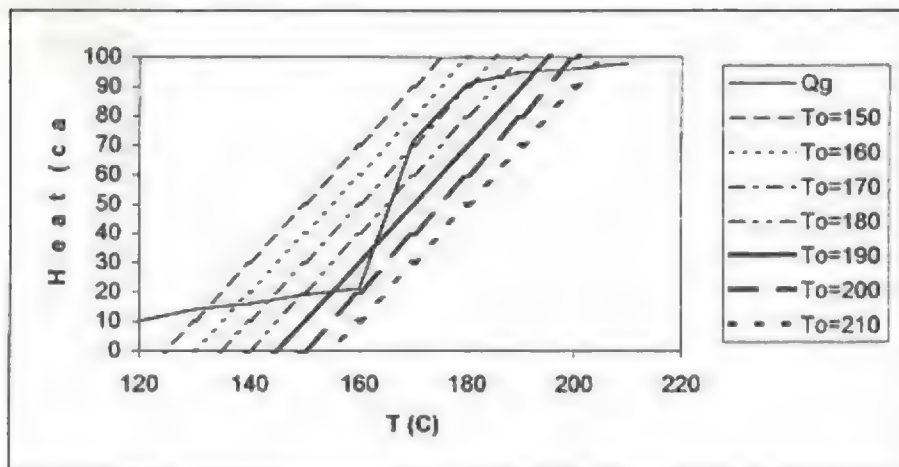
The equation for heat removal curve is:

$$Q_R = F_{A0} C_{pA} (T - T_0) + UA(T - T_A) = (0.5)(2) (T - T_0) + (1.0) (T - 100)$$

$$Q_R = 2T - T_0 - 100 \quad (5)$$

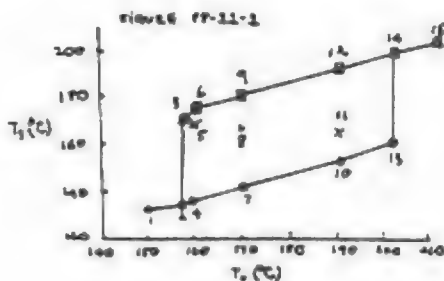
Plot this along with the heat generation curve for various T_0 . This is shown in Figure P8-22-1.

8-60



The intersection between Q_g and Q_r can be used to prepare the ignition - extinction curve shown in figure P8-22-2. The values for T_s as a function of inlet temperature, T_0 , are tabulated below.

T_0 (°C)	T_s (°C)
150	132
157	135, 172
160	137, 168, 176
170	142.5, 167, 181
190	154.5, 165, 193.5
202	162, 199
210	204.5



- To obtain high conversion, the reactor must operate at or beyond point 14 in figure P-22-2. So the minimum inlet temperature for high conversion is $T_0 \geq 202$ °C.
- The temperature of the fluid in the reactor corresponding to temperature in part 1 is $T_s \geq 199$ °C (point 14 in figure P8-22-2).
- The inlet temperature of the fluid is $T_0 = 202 + 5 = 207$ °C. This will be somewhere between points 14 and 15 in figure P8-22-2. Once the fluid is cooled from this temperature, it will follow the line formed by points 15, 14, 12, 9, etc.. Now $T_0 = 207 - 10 = 197$ °C. From figure P8-22-2, $T_s = 195.5$ °C. From equation (5),

P8-21 (cont'd)

$Q_R = 2 \times 1965 - 197 - 100 = 96 \text{ cal/min.}$ Now since at intersection point

$Q_R = Q_S$, so $Q_S = 96 \text{ cal/min}$ From equation (4): $X = \frac{Q_S}{100} = 0.96$

d) Extinction temperature is the temperature corresponding to point 3 in figure P-22-2:
 $T_{ext} = 157^\circ\text{C}.$

e) No solution will be given

P8-22

$$F_{AO} X = -r_A V = k C_{AO} \left(1 + \frac{1}{K_e}\right) X V = C_{AO} v_0 X$$

$$\tau k \left(1 + \frac{(K_e + 1)}{K_e}\right) X = X$$

$$\frac{\tau k}{1 + \tau k \frac{(K_e + 1)}{K_e}} = X$$

$$\frac{\tau K}{1 + \tau K \left[\frac{K_e + 1}{K_e}\right]} = X$$

$$G(T) = \frac{(-r_A)(-\Delta H)}{F_{AO}} = X(-\Delta H_R) = 80,000 X$$

$$R(T) = C_{PA} (1 + K) [T - T_c]$$

$$T_c = \frac{T_0 + K T_A}{1 + K}, K = \frac{UA}{F_{AO} C_{PA}} = \frac{2000}{(10)(40)} = 5$$

$$T_c = \frac{300 + (5)(313)}{6} = 311$$

$$R(T) = (40)(1 + 5)(T - 311) = 240 [T - 311]$$

$$k = .001 \exp\left(\frac{150,000}{8.31} \left(\frac{1}{373} - \frac{1}{T}\right)\right) = 0.001 \exp\left[18.051 \left(\frac{1}{373} - \frac{1}{T}\right)\right]$$

$$K = 100.0 \exp\left(\frac{80,000}{8.31} \left(\frac{1}{350} - \frac{1}{T}\right)\right) = 100 \exp\left[9.267 \left(\frac{1}{350} - \frac{1}{T}\right)\right]$$

$$\tau = \frac{V}{v_0}$$

$$X = \tau K$$

Multiple Steady States

Equations:

$$\frac{dT}{dz} = 2$$

$$z = 100$$

$$k = 0.001 \exp(18.051 \cdot (1/373 - 1/T))$$

$$K = 100 \exp(-9.267 \cdot (1/350 - 1/T))$$

$$T = 300$$

$$T = 313$$

$$T_c = (T_0 + K T_A) / 6$$

$$k = 0.001 \exp(18.051 \cdot (1/373 - 1/T))$$

$$K = 100 \exp(-9.267 \cdot (1/350 - 1/T))$$

$$T_c = 300$$

$$T_c = 313$$

$$T_c = 311$$

$$T_c = 311$$

$$T_c = 311$$

$$T_c = 311$$

Variable

z

T

tau

k

ke

To

Ta

Tc

X

r

g

Initial value

Maximum value

Minimum value

Final value

0

100

0

100

300

500

300

500

100

100

100

100

7.68763e-09

217.968

7.68763e-09

217.968

8250.49

8250.49

0.0355089

0.0355089

300

300

300

300

313

313

313

313

310.833

310.833

310.833

310.833

7.68762e-07

0.631768

7.68762e-07

0.0342912

-2600

45400

-2600

45400

0.061501

50541.4

0.061501

2743.29

$$\tau = 100$$

$$T_0 = 300$$

$$T_A = 313$$

$$T_c = 311$$

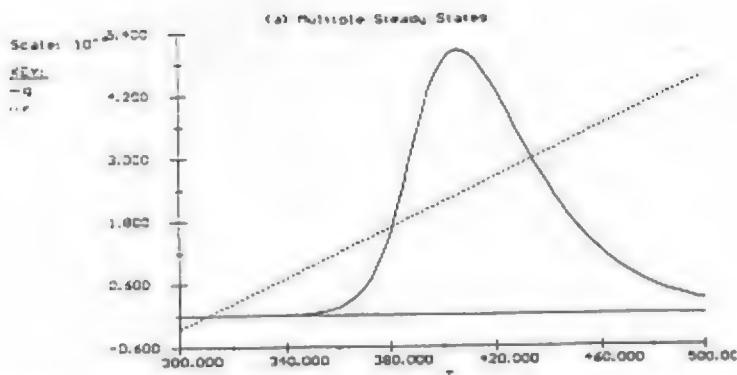
$$T_c = 311$$

$$T_c = 311$$

$$T_c = 311$$

$$T_c = 311$$

8-62



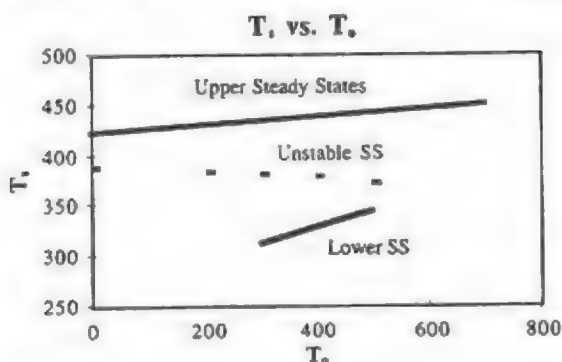
- (b) Vary T_a to determine the effect on the number of steady states:

For $T_a > 367$, there is only one steady-state.

For $300 < T_a < 367$, there are three.

For $T_a < 300$, there are only two.

- (c) Vary T_o and record all T_s 's. Use these data to generate a plot of T_s vs. T_o . From this graph determine the ignition and extinction temperatures.



From this it is apparent that the extinction temperature is 235° F and the ignition temperature is 562° F.

- (d)

For $K_e = \infty$,

$$X = \frac{\tau k}{1 + \tau k \left(\frac{\infty + 1}{\infty} \right)} = \frac{\tau k}{1 + \tau k}$$

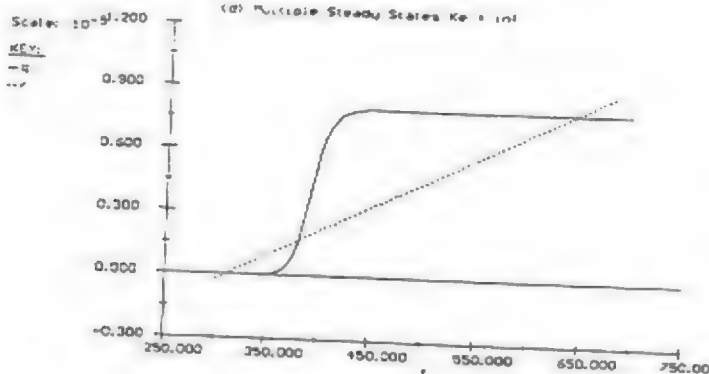
$$= \frac{\tau k}{1 + \tau k \left[\frac{k_e + 1}{k_e} \right]} \xrightarrow{k_e \rightarrow \infty} \frac{\tau k}{1 + \tau k \left[1 + \frac{1}{k_e} \right]} \rightarrow \frac{\tau k}{1 + \tau k}$$

Use the same POLYMATH program, but with this new equation for X , to produce the desired graphs.

(d) Multiple Steady States $K_e = \infty$

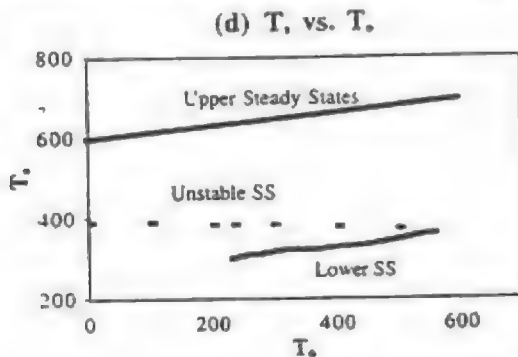
Equations:

	Variable	Initial value	Maximum value	Minimum value	Final value
$d(T)/d(z)=2$	z	0	200	0	200
$\tau=100$	T	300	700	300	700
$k=0.001 \cdot \exp(18051 \cdot (1/373 - 1/T))$	τ	100	100	100	100
$k_e=100 \cdot \exp(-9267 \cdot (1/350 - 1/T))$	k	$7.68763e-09$	$6.57775e+06$	$7.68763e-09$	$6.57775e+06$
$T_o=300$	k_e	8250.49	8250.49	0.000178058	0.000178058
$T_a=313$	T_o	300	300	300	300
$T_c=(T_o+5 \cdot T_a)/6$	T_a	313	313	313	313
$X=\tau \cdot k / (1 + \tau \cdot k)$	T_c	310.833	310.833	310.833	310.833
$r=240 \cdot (T - T_c)$	X	$7.68762e-07$	1	$7.68762e-07$	1
$g=80000 \cdot X$	r	-2600	93400	-2600	93400
$f=g-r$	g	0.061501	80000	0.061501	80000
$z_0 = 0, \quad z_f = 200$	f	2600.06	50510.4	-13400	-13400



Repeat parts (b) and (c) for this new situation:

By varying T_s , the following data were obtained:For $T_s > 367$, there is 1 steady state.For $367 > T_s > 60$, there are three steady states.For $T_s < 60$, there is only one steady state.For $T_s = 367$ and 60, there are two steady states.By varying T_o , the following graph was generated:



From this we can see that the extinction temperature is 235°F and the ignition temperature is 562°F. Note that these are the same values as above.

P8-23

(a)

Initial Calculations:

For 1 inch schedule 40 pipe, $D = 1.049 \text{ in} = 0.0266 \text{ m}$

$$V = \pi D^2 L = \pi (0.0266 \text{ m})^2 (10 \text{ m}) = 0.0223 \text{ m}^3$$

$$F_{A0} = (6000 \text{ kg/hr}) \left(\frac{1000 \text{ g}}{\text{kg}} \right) \left(\frac{1 \text{ mol}}{58 \text{ g}} \right) \left(\frac{1 \text{ hr}}{3600 \text{ s}} \right) = 28.736 \text{ mol/s}$$

Dividing this into 1000 tubes, $F_{A0} = 0.0287 \text{ mol/s}$

To develop our Design Equation, we must use the data given in Example 8-7.

Mole Balance : $\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$

Rate Law : $-r_A = kC_A$

Stoichiometry : $C_A = \frac{C_{A0}(1-X)T_o}{(1+\epsilon X)T}$ $\epsilon = y_{A0}\delta = y_{A0}$

$$C_{A0} = \frac{P_o}{RT_o} y_{A0} = 57.276 y_{A0}$$

$$y_{A0} = \frac{F_{A0}}{F_{T0}} = \frac{F_{A0}}{F_{A0} + F_{N_2,0}} = \frac{F_{A0}}{F_{A0} + \Theta_{N_2} F_{A0}} = \frac{F_{A0}}{\Theta_{N_2} (1 + F_{A0})}$$

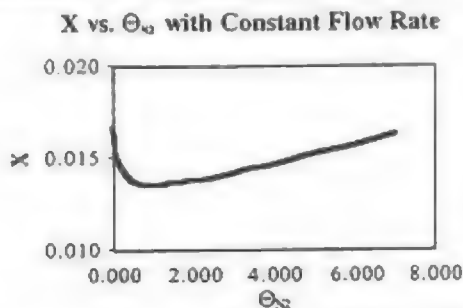
Energy Balance:
$$\frac{dT}{dV} = \frac{-r_A(-\Delta H_{Rx})}{F_{Ao}(C_{pA} + \Theta_{N_2} C_{pN_2} + X \Delta C_p)}$$

$$-\Delta H_{Rx} = 80,770 + 6.8(T - T_R) - 5.75 \times 10^{-3}(T^2 - T_R^2) - 1.27 \times 10^{-6}(T^3 - T_R^3)$$

$$C_{pN_2} = 4.19(6.50 + 0.001T) \quad C_{pA} = 26.63 + 0.183T + 45.86 \times 10^{-6}T^2$$

$$\Delta C_p = 6.8 - 11.5 \times 10^{-3}T - 3.81 \times 10^{-6}T^2$$

Use these equations in POLYMATH. Vary F_{N_2} , while keeping F_{T_0} constant to generate a graph of X vs. Θ_{N_2} .



P8-23 (a) Constant Flow Rate

Equations:

$$\frac{dT}{dV} = -r_A \frac{\Delta H_{Rx}}{F_{Ao}(C_{pA} + \Theta_{N_2} C_{pN_2} + X \Delta C_p)}$$

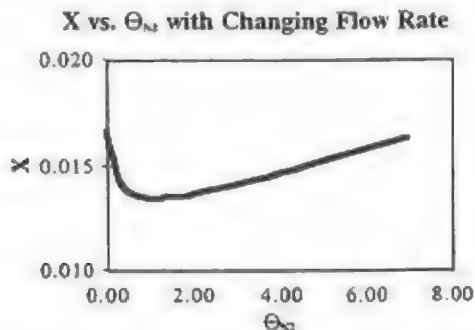
$$\frac{dX}{dV} = -r_A / F_{Ao}$$

$k = 0.2 \times 10^4 \exp(-34222/T)$ $\rightarrow k$
 $C_{pA} = 26.63 + 0.183T + 45.86 \times 10^{-6}T^2$ $\rightarrow C_{pA}$
 $C_{pN_2} = 4.19(6.50 + 0.001T)$ $\rightarrow C_{pN_2}$
 $\Delta C_p = 6.8 - 11.5 \times 10^{-3}T - 3.81 \times 10^{-6}T^2$ $\rightarrow \Delta C_p$
 $f_{N_2} = 0.0286$ $\rightarrow f_{N_2}$
 $T_0 = 1050$ $\rightarrow T_0$
 $T_R = 298$ $\rightarrow T_R$
 $\Delta H_{Rx} = 80770 + 6.8(T - T_R) - 5.75 \times 10^{-3}(T^2 - T_R^2) - 1.27 \times 10^{-6}(T^3 - T_R^3)$ $\rightarrow \Delta H_{Rx}$
 $\Theta_{N_2} = f_{N_2} / (1 - f_{N_2})$ $\rightarrow \Theta_{N_2}$
 $Y_{Ao} = f_{N_2} / (1 - f_{N_2})$ $\rightarrow Y_{Ao}$
 $C_{Ao} = Y_{Ao} / (1 - Y_{Ao})$ $\rightarrow C_{Ao}$
 $C_A = C_{Ao} (1 - X)$ $\rightarrow C_A$

Variable	Initial value	Maximum value	Minimum value	Final value
V	0	0.0223	0	0.0223
T	1050	1050	1037.34	1037.34
X	0	0.0207844	0	0.0207844
k	5.74279	5.74279	3.85847	3.85847
CpA	269.342	269.342	265.813	265.813
CpN2	31.6345	31.6345	31.5815	31.5815
delcp	-9.47552	-9.22931	-9.47552	-9.22931
fN2	0.0286	0.0286	0.0286	0.0286
To	1050	1050	1050	1050
Tr	298	298	298	298
delh	-5.7443e-06	-5.59243e-06	-5.7443e-06	-5.59243e-06
fao	0.0001	0.0001	0.0001	0.0001
thetan	286	286	286	286
yao	3.49615e-07	3.49615e-07	3.49615e-07	3.49615e-07
cao	2.00246e-05	2.00246e-05	2.00246e-05	2.00246e-05
ca	2.00246e-05	2.00246e-05	1.98476e-05	1.98476e-05

(b)

Use the same equations in POLYMATH, but this time vary F_{N20} while keeping F_{A0} constant, allowing the overall flow rate (F_{T0}) to change.



P8-23 (b) Changing Flow Rate

Equations:

$$d(T)/d(V) = -ra \cdot \text{delh} / (fao \cdot (cpa + \text{thetan} \cdot \text{cpn} + X \cdot \text{delcp}))$$

$$d(X)/d(V) = -ra / fao$$

$$k = 8.2e14 \cdot \exp(-34222/T)$$

$$fao = 0.0287$$

$$cpa = 26.63 + 0.183 \cdot T + 45.86e-6 \cdot T^2$$

$$\text{cpn} = 4.19 \cdot (6.50 + 0.001 \cdot T)$$

$$\text{delcp} = 6.8 - 11.5e-3 \cdot T - 3.81e-6 \cdot T^2$$

$$\text{fn} = 0.01144$$

$$To = 1050$$

$$Tr = 298$$

$$\text{delh} = 80770 + 6.8 \cdot (T - Tr) - 5.75 \cdot (T^2 - Tr^2) - 1.27e-6 \cdot (T^3 - Tr^3)$$

*3)

$$\text{thetan} = \text{fn} / fao$$

$$\text{yao} = fao / \text{thetan} / (fao + 1)$$

$$\text{cao} = 57.276 \cdot \text{yao}$$

$$\text{ca} = \text{cao} \cdot (1 - X) \cdot To / (1 + \text{yao} \cdot X) / T$$

$$ra = -k \cdot \text{ca}$$

$$V_0 = 0, \quad V_f = 0.0223$$

Initial value

1050

0

Variable	Initial value	Maximum value	Minimum value	Final value
V	0	0.0223	0	0.0223
T	1050	1050	828.919	828.919
X	0	0.0134562	0	0.0134562
k	5.74279	5.74279	0.000963674	0.000963674
fao	0.0287	0.0287	0.0287	0.0287
cpa	269.341	269.341	209.833	209.833
cpn	31.6345	31.6345	30.7082	30.7082
delcp	-9.47552	-5.35045	-9.47552	-5.35045
fn	0.0287	0.0287	0.0287	0.0287
To	1050	1050	1050	1050
Tr	298	298	298	298
delh	-5.7443e+06	-3.35655e+06	-5.7443e+06	-3.35655e+06
thetan	1	1	1	1
yao	0.0278993	0.0278993	0.0278993	0.0278993
cao	1.59796	1.59796	1.59796	1.59796
ca	1.59796	1.99616	1.59796	1.99616

8-67

P8-24

No solution will be given.

P8-25



Liquid phase

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

$$-r_A = k C_A C_B$$

$$k = .01 * \exp\left(-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{300}\right)\right)$$

$$C_A = C_{A0}(1 - X) = C_B$$

The energy balance is next.

$$\frac{dT}{dV} = \frac{Ua(T_s - T) + (-r_A)(-\Delta H_R)}{F_{A0}[C_{pA} + C_{pB}]}$$

$$a = \frac{4}{D}$$

assume $D = 4$

$$U = \frac{5J}{m^2 Ks} \left(\frac{1 cal}{4.1841J} \right) \left(\frac{1 m^2}{10^3 dm^2} \right) = .0120 \frac{cal}{dm^2 Ks}$$

Plug those into POLYMATH to come up with these two graphs of conversion and temperature.

Equations:

$$d(x)/d(v) = -ra/fao$$

$$d(T)/d(v) = (U*a*(Ta-T) + (-ra)*(-Dhr1)) / (fao*(cpa+cpb))$$

$$D = .0120$$

$$a = 1$$

$$Ts = 300$$

$$Dhr1 = -6000$$

$$fao = .2$$

$$cpa = 15$$

$$cpb = 15$$

$$E = 10000$$

$$R = 1.987$$

$$cao = .1$$

$$ca = cao*(1-x)$$

$$cb = cao*(1-x)$$

$$k = .01 * \exp(-E/R*(1/T - 1/300))$$

$$ra = k*ca*cb$$

$$v_0 = 0, \quad v_f = 1000$$

Initial value

0

300

Variable

Initial value

Maximum value

Minimum value

Final value

v

0

1000

0

1000

x

0

0.962152

0

0.962152

T

300

434.882

300

346.181

U

0.012

0.012

0.012

0.012

a

1

1

1

1

Ta

300

300

300

300

Dhr1

-6000

-6000

-6000

-6000

fao

0.2

0.2

0.2

0.2

cpa

15

15

15

15

cpb

15

15

15

15

E

10000

10000

10000

10000

R

1.987

1.987

1.987

1.987

cao

0.1

0.1

0.1

0.1

ca

0.1

0.1

0.00378482

0.00378482

cb

0.1

0.1

0.00378482

0.00378482

k

0.01

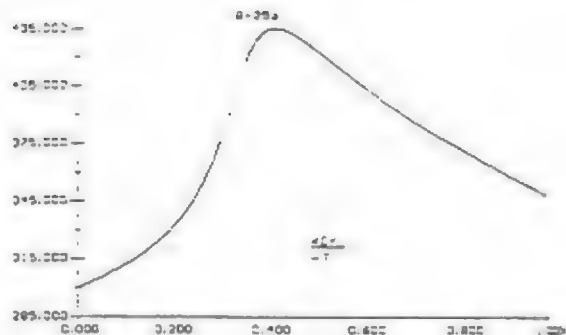
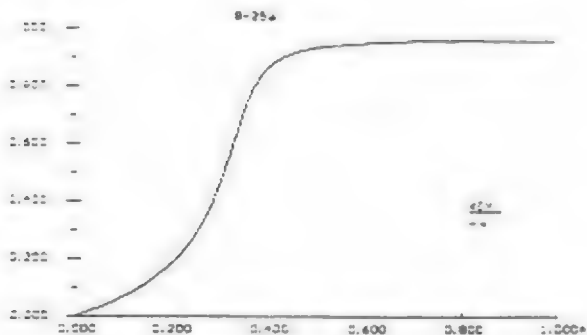
1.81836

0.01

0.1019

8-68

P8-25 cont'd



b) Gas-phase reaction



The design equation for a PBR is then:

$$\frac{dX}{dW} = \frac{-r_A}{F_{A0}}$$

$$-r_A = kC_A$$

$$C_A = \frac{C_{A0}(1-X)T_0}{1+X} \frac{T}{T_0}$$

$$k = .133 * \exp\left(\frac{E}{R}\left(\frac{1}{450} - \frac{1}{T}\right)\right)$$

$$C_{A0} = \frac{P}{RT} = \frac{10}{(0.082)(450)} = .27 \frac{\text{mol}}{\text{dm}^3}$$

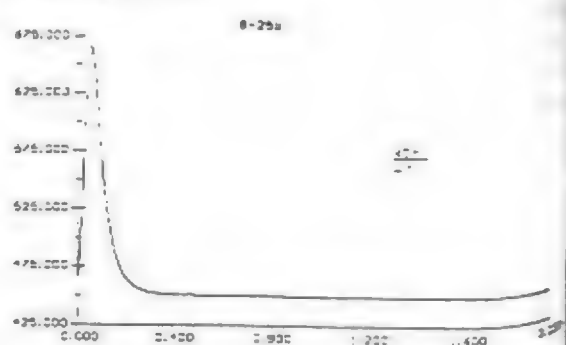
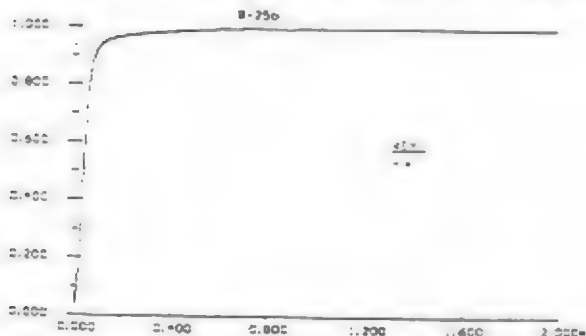
Then the energy balance:

$$\frac{dT}{dW} = \frac{Ua(T_s - T) + (-r_A)(-\Delta H_R)}{F_{A0} * C_{pA}}$$

$$\Delta H_R = -40 - 50 + 70 = -20 \text{ kJ/mol}$$

$$U = 5$$

Plug those into POLYMATH gives the following graphs:



P8-25 cont'd

8-25b

Equations:

$$d(x)/d(w) = -r_a/f_{ao}$$

$$d(T)/d(w) = (U \cdot a \cdot (T_a - T) + (-r_a) \cdot (-D_{hr})) / (f_{ao} \cdot c_{pa})$$

$$U = 5$$

$$a = 1$$

$$T_a = 450$$

$$D_{hr} = -20000$$

$$f_{ao} = 5.4$$

$$c_{pa} = 40$$

$$E = 31400$$

$$R = 8.3144$$

$$c_{ao} = .27$$

$$T_o = 450$$

$$c_a = (c_{ao} \cdot (1-x) \cdot T_o) / ((1+x) \cdot T)$$

$$k = .133 \cdot \exp(E/R \cdot (1/450 - 1/T))$$

$$r_a = -k \cdot c_a$$

$$w_o = 0, \quad w_f = 2000$$

Initial value

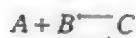
0

450

8-25b

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	2000	0	2000
x	0	0.999924	0	0.999924
T	450	665.963	450	450.006
U	5	5	5	5
a	1	1	1	1
Ta	450	450	450	450
Dhr	-20000	-20000	-20000	-20000
fao	5.4	5.4	5.4	5.4
cpa	40	40	40	40
E	31400	31400	31400	31400
R	8.3144	8.3144	8.3144	8.3144
cao	0.27	0.27	0.27	0.27
To	450	450	450	450
ca	0.27	0.27	1.02394e-05	1.02394e-05
k	0.133	2.0221	0.133	0.133016
ra	-0.01591	-1.362e-06	-0.093202	-1.362e-06

c) Gas-phase



Use the design equation:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

$$-r_A = k \left[C_A C_B - \frac{C_C^2}{K_r} \right]$$

$$C_A = C_{A0} (1 - X) \frac{T_o}{T}$$

$$C_B = C_{A0} (1 - X) \frac{T_o}{T}$$

$$C_C = 2 C_{A0} X \frac{T_o}{T}$$

$$k = .035 \cdot \exp \left[\frac{E}{R} \left(\frac{1}{273} - \frac{1}{T} \right) \right]$$

$$K_r = 25000 \cdot \exp \left[\frac{\Delta H_R}{R} \left(\frac{1}{298} - \frac{1}{T} \right) \right]$$

$$C_T = \frac{P}{RT} = \frac{580.5}{(8.309)(350)} = .2$$

$$C_A = .5 \cdot .2 = .1$$

8-70

P8-25 cont'd

Then use the energy balance:

$$\frac{dT}{dV} = \frac{Ua(T_o - T) + (-r_A)(-\Delta H_R)}{F_{A0}(C_{pA} + C_{pB})}$$

$$\Delta H_R = -90 + 40 + 30 = -20$$

Plug those into POLYMATH and get the following graphs.

8-25c

Equations:

$$d(x)/d(v) = -ra/fao$$

$$d(T)/d(v) = (U*a*(T_o - T) + (-ra)*(-Dhrl)) / (fao*(cpa + cpb + Dcp))$$

$$U = 5$$

$$a = 1$$

$$T_o = 350$$

$$Dhrl = -20000$$

$$fao = 20$$

$$cpa = 25$$

$$cpb = 15$$

$$Dcp = 0$$

$$E = 70000$$

$$R = 8.3144$$

$$cao = .1$$

$$T_o = 350$$

$$k = .035 * \exp(E/R * (1/273 - 1/T))$$

$$ca = cao * (1 - x) * T_o / T$$

$$cc = 2 * cao * x * T_o / T$$

$$K = 25000 * \exp(Dhrl/R * (1/298 - 1/T))$$

$$cb = ca$$

$$ra = -k * (ca * cb - cc^2 / K)$$

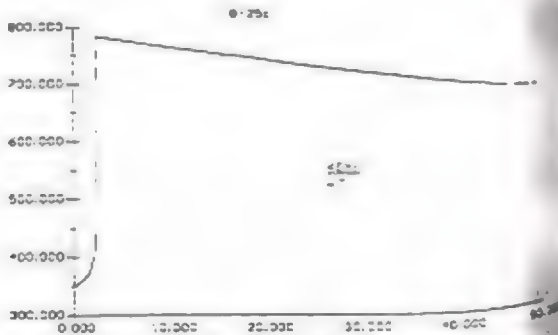
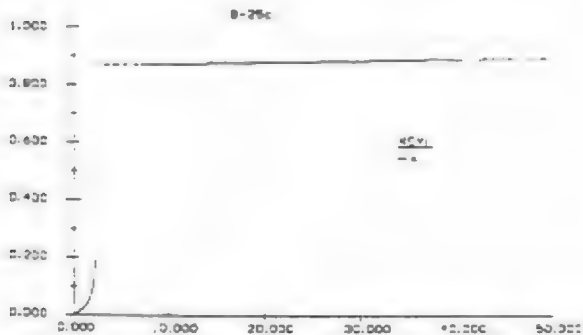
$$v_0 = 0, \quad v_f = 50$$

Initial value

0

350

Variable	Initial value	Maximum value	Minimum value	Final value
v	0	50	0	50
x	0	0.890645	0	0.890645
T	350	782.841	350	682.116
U	5	5	5	5
a	1	1	1	1
Ta	350	350	350	350
Dhrl	-20000	-20000	-20000	-20000
fao	20	20	20	20
cpa	25	25	25	25
cpb	15	15	15	15
Dcp	0	0	0	0
E	70000	70000	70000	70000
R	8.3144	8.3144	8.3144	8.3144
cao	0.1	0.1	0.1	0.1
To	350	350	350	350
k	30.9458	1.84821e+07	30.9458	3.7762e+06
ca	0.1	0.1	0.00561108	0.00561108
cc	0	0.0913997	0	0.0913997
X	7535.33	7535.33	168.568	265.357
cb	0.1	0.1	0.00561108	0.00561108
ra	-0.309458	-0.00928109	-1059.19	-0.00928109



Tabulation of Results

$T_0 = 1360$			$T_0 = 1370$		
X	I	Z	X	I	Z
0.050	1386.4	219.6	0.050	1396.3	99.4
0.100	1412.7	252.8	0.100	1422.6	114.9
0.150	1438.9	259.2	0.150	1448.9	117.9
0.200	1465.1	260.4	0.200	1475.0	118.5
0.250	1491.2	260.6	0.250	1501.2	118.7
0.300	1517.3	260.6	0.300	1527.2	118.7
0.350	1543.3	260.6	0.350	1553.2	118.7
0.400	1569.2	260.6	0.400	1579.1	118.7
0.450	1595.1	260.6	0.450	1605.0	118.7
0.500	1620.9	260.6	0.500	1630.8	118.7
0.525	1633.8	260.6	0.524	1643.2	118.7
0.533	1637.9	260.6			

```

C W=CATALYST WEIGHT          AC=CROSS SECTIONAL AREA
C R=REACTOR RATE             AK1=SPECIFIC REACTION RATE
C T=TEMPERATURE              AKE=EQUILIBRIUM CONSTANT
C X=CONVERSION               DX=INCREMENT IN CONVERSION
C Z=DISTANCE DOWN THE REACTOR RHO=BULK DENSITY
C FAD=ENTERING MOLAR FLOW RATE OF A
C PFREQ=PRINTING FREQUENCY
      INTEGER PFREQ
      WRITE (5,10)
10  FORMAT('ENTER VALUES OF T0,FAD,AC,RHO,DX,PFREQ SEPARATED BY COMMAS'/
     & 'EXAMPLE: / 1370.,.00105.,.196.,192.,.00125./')
      READ (5,20) T0, FAD, AC, RHO, DX, PFREQ
20  FORMAT(5F10.5,15)
      WRITE (5,30)
30  FORMAT('1',9X,'T0',16X,'FAD',12X,'AC',11X,'RHO',14X,'DX'/)
      WRITE (5,40) T0, FAD, AC, RHO, DX
40  FORMAT(5X,5F15.5//)
      WRITE (5,50)
50  FORMAT(5X,'X',16X,'T',16X,'AK1',12X,'AKE',12X,'R',14X,'W',14X,'Z'/)
      |
      XI = 0.0
      X = 0.0
      W = 0.0
      IFREQ = -1
50  CONTINUE
C CALCULATE ADIABATIC TEMPERATURE
      T = (43260./X + 77.3)/T0 / (1.8/X + 77.3)
C CALCULATE SPECIFIC REACTION RATE & EQUILIBRIUM CONSTANT AT THIS
C TEMPERATURE
      AK1 = EXP(92.5 - 149750./T)
      AKE = EXP(42300./T - 24.2 + 0.17*LOG(T))
C CALCULATE RATE OF REACTION
      IF (X .GT. 0.05) GO TO 70
      R = AK1 * (0.4292 - 0.01176/AKE)
      GO TO 80
70  R = AK1 * SQRT((1. - X)/X) * ((.91 - .50X)/(9.1 - .50X) - (X/(1. -
     & 1.X))**.2/AKE)
C CALCULATE THE CATALYST WEIGHT AND REACTOR LENGTH
C NECESSARY TO ACHIEVE THIS CONVERSION.
      W = W + FAD * (X - XI) / R
      Z = W / RHO / AC
      IFREQ = IFREQ + 1
      IF (IFREQ .NE. PFREQ) GO TO 95
      IFREQ = 0
      WRITE (6,90) X, T, AK1, AKE, R, W, Z
      GO TO 100
90  FORMAT(1X,1P7E15.5)
C CHECK TO SEE IF EQUILIBRIUM HAS BEEN REACHED
      95 IF (R .LE. 0.0) GO TO 100
C INCREMENT X AND THEN REPEAT THE CALCULATIONS AS NECESSARY
      XI = X
      X = X + DX
      GO TO 60
100 WRITE(6,90) X, T, AK1, AKE, R, W, Z
      END

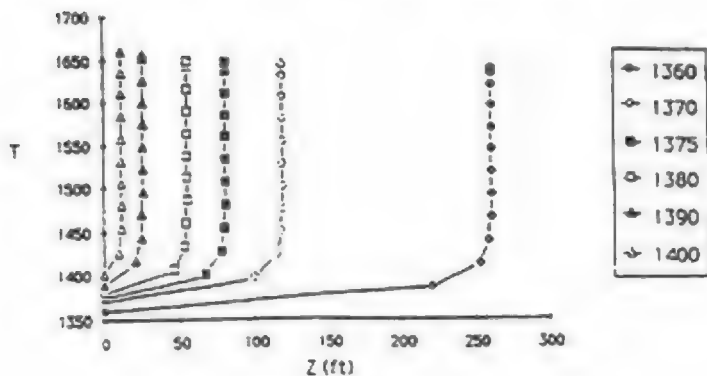
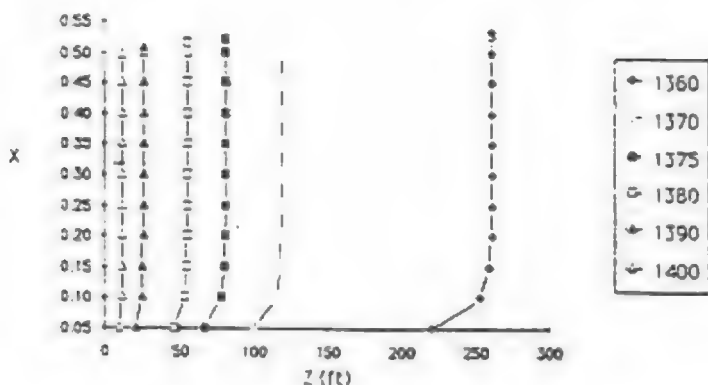
```

$T_0 = 1375$		
X	I	Z
0.050	1401.3	67.15
0.100	1427.6	77.79
0.150	1453.9	79.92
0.200	1480.0	80.34
0.250	1506.1	80.42
0.300	1532.2	80.44
0.350	1558.2	80.45
0.400	1584.1	80.45
0.450	1609.9	80.45
0.500	1635.8	80.45
0.520	1646.1	80.45

$T_0 = 1380$		
X	I	Z
0.050	1406.3	45.49
0.100	1432.6	52.82
0.150	1458.9	54.31
0.200	1485.0	54.60
0.250	1511.1	54.66
0.300	1537.1	54.68
0.350	1563.1	54.68
0.400	1589.0	54.68
0.450	1614.9	54.68
0.500	1640.7	54.68
0.515	1648.4	54.68

$T_0 = 1390$		
X	I	Z
0.050	1416.3	21.06
0.100	1442.6	24.56
0.150	1468.8	25.29
0.200	1494.9	25.43
0.250	1521.0	25.46
0.300	1547.1	25.47
0.350	1573.0	25.47
0.400	1598.9	25.47
0.450	1624.8	25.47
0.500	1650.6	25.47
0.506	1653.7	25.47

$T_0 = 1400$		
X	I	Z
0.050	1426.3	9.8
0.100	1452.6	11.5
0.150	1478.8	11.9
0.200	1504.9	12.0
0.250	1530.9	12.0
0.300	1557.0	12.0
0.350	1583.0	12.0
0.400	1608.9	12.0
0.450	1634.7	12.0
0.497	1659.0	12.0



P8-26 (cont'd)

- Comments:
- X and T increase with Z
 - Exothermic
 - Reaction front increases for decreasing T_0

From data

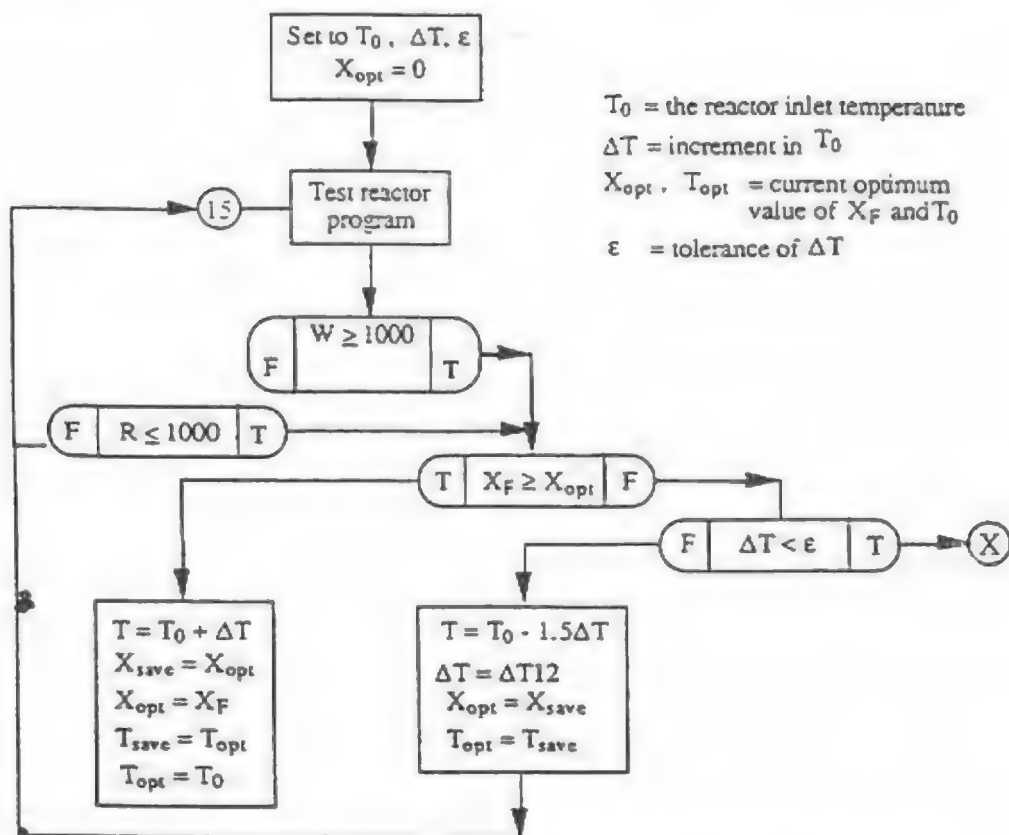
<u>Reaction front (ft)</u>	<u>T_0 (°K)</u>	<u>X (final)</u>
37834.60	1300	0.589
260.60	1360	0.533
118.70	1370	0.524
80.45	1375	0.520
54.68	1380	0.515
25.47	1390	0.506
12.00	1400	0.497
5.72	1410	0.488
2.75	1420	0.479
2.62×10^{-5}	1600	0.324

To obtain "best" T_0 , we would have to examine conversion, reaction front and catalyst weight, then weigh these factors to find the one where all is satisfied to a good extent.

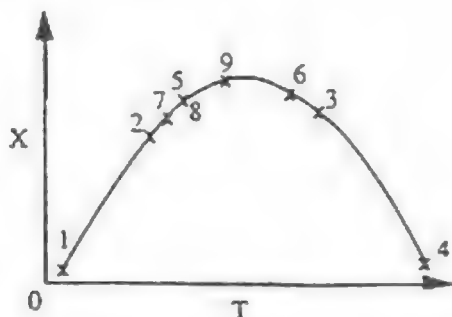
P8-27

Because the reaction is exothermic, the final equilibrium conversion will decrease in temperature. So long as X_F , the final conversion for a reactor with $W = 1000\text{lb}$, is much less than X_e , the equilibrium conversion at the outlet, an increase in T_0 should increase X_F at the point where $X_F = X_e$, however, any increase in temperature should decrease X_F . It appears, therefore, that a unique maximum conversion for X_F with respect to T exist and may be found by starting with a low value of T_0 and increase T_0 until X_F no longer increases.

First, an additional exist statement to the program should be added so that computation ceases when $W \geq 1000\text{ lb}$. Proposed modifications to the program are shown below.



In this scheme, T_0 is increased as long as X_F is increased. The maximum value of X_F is set at X_{opt} if X_F is greater than the previously calculated value of X_F . Once $X_{opt} > X_F$, T_0 is incremented to a value below the current optimum point, ΔT is decreased and T_{opt} and X_{opt} are reset. The process continues with T_0 jumping past the previously calculated T_{opt} until ΔT is decremented below some tolerance ϵ . This process is illustrated below with the points numbered in sequential order. Note that part 5 and 8 are one and the same sequences of calculations of proposed program.



8-75

Mole balances:

$$V = \frac{F_{A0} - F_A}{-r_A}$$

$$V = \frac{F_B}{r_B} = \frac{F_C}{r_C}$$

rate laws:

$$-r_A = k_1 C_A$$

$$r_B = k_1 C_A - k_2 C_B$$

$$r_C = k_2 C_B$$

Stoichiometry:

$$C_i = \frac{F_i}{v_0} \frac{T}{T_0}$$

$$F_B = 10F_C$$

$$.5 = \frac{.05 - F_A}{0.5}$$

$$F_A = .025$$

$$11F_C = .025$$

$$F_C = .023 \quad F_B = .023$$

From this we can use two of the mole balances to solve for T

$$\frac{F_{A0} - F_A}{k_1 F_A} = \frac{F_C}{k_2 F_B}$$

$$\frac{1}{A_1 e^{-E/RT}} = \frac{0.1}{A_2 e^{-E/RT}}$$

$$T = 269^\circ F$$

Knowing the temperature we can then solve for the Volume:

$$V = \frac{F_B v_0}{k_1 F_A - k_2 F_B} \frac{T_0}{T} = 11.9 \text{ ft}^3$$

We then need the energy balance:

$$UA(T_a - T) - F_{A0} C_{pa} (T - T_0) + V[(\Delta H_{R1})(r_{1A}) + \Delta H_{R2}(r_{2B})] = 0$$

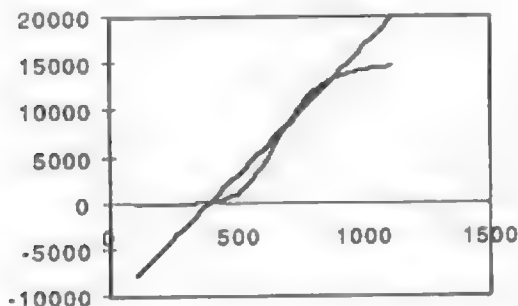
P8-28 cont'd

Solve for A and we get:

$$A = 399 \text{ ft}^2$$

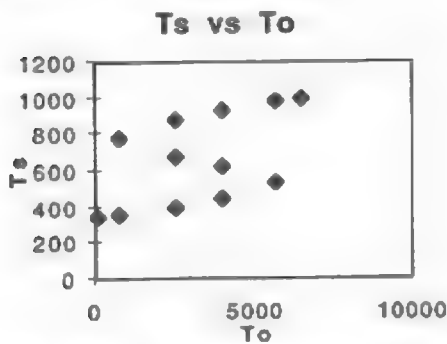
d) In order to get multiple steady-states, the kappa, tau and feed temperature had to be changed. $\kappa = 0.1$, $\tau = 0.0005$ and T_0 would be changed around.

This first graph is $G(T)$, $R(T)$ vs T at $T_0 = 2000^\circ\text{F}$



As can be seen there are three steady-states.

The next graph is of T_s vs. T_0 .





Mole Balances: $\frac{dF_A}{dW} = r_A$ $\frac{dF_B}{dW} = r_B$ $\frac{dF_C}{dW} = r_C$

Rate laws:

$$r_A = -r_{2B} + r_{1A} + r_{3A}$$

$$r_B = -r_{1A} + r_{2B}$$

$$r_C = -r_{3A}$$

$$-r_{1A} = k_1 C_A$$

$$-r_{2B} = k_2 C_B$$

$$-r_{3A} = k_3 C_C$$

Stoichiometry:

$$C_A = C_T \frac{F_A}{F_T} \frac{T_0}{T} \quad C_B = C_T \frac{F_B}{F_T} \frac{T_0}{T}$$

Energy Balance:

$$\frac{dT}{dW} = \frac{Ua(T_A - T) + (-r_{1A})(-\Delta H_{R1A}) + (-r_{2B})(-\Delta H_{R2B}) + (-r_{3A})(-\Delta H_{R3A})}{F_A C_{pA} + F_B C_{pB} + F_C C_{pC}}$$

$$\frac{dT}{dW} = \frac{16(500 - T) + 1800(-r_{1A}) - 1800(-r_{2B}) + 1100(-r_{3A})}{100(F_A + F_B + F_C)}$$

Evaluate the parameters.

$$k_1 = 0.5 \exp[2(1 - 320/T)]$$

$$k_2 = \frac{k_1}{K_C}$$

$$k_3 = 0.005 \exp[4.6(1 - 460/T)]$$

$$K_C = 10 \exp[4.8(430/T - 1.5)]$$

Plug those into POLYMATH and the following program is created.

Equations:

$$d(fb)/d(w) = r_b$$

$$d(fa)/d(w) = r_a$$

$$d(fc)/d(w) = r_c$$

$$d(T)/d(w) = (Ua \cdot (Ta - T) - (r_{1a}) \cdot (-\Delta H_{r1a}) - (r_{2b}) \cdot (-\Delta H_{r2b}) - (r_{3a}) \cdot (-\Delta H_{r3a})) / (fa \cdot cpa + fb \cdot cpb + fc \cdot cpc)$$

$$Ua = 16$$

$$Ta = 500$$

$$\Delta H_{r1a} = -1800$$

$$\Delta H_{r3a} = -1100$$

$$cpa = 100$$

$$cpb = 100$$

$$cpc = 100$$

$$k1 = 0.5 \cdot \exp[2 \cdot (1 - 320/T)]$$

Initial value

1

1

0

330

8-78

P8-29cont'd

```
x3=.005*exp(4.6*(1-1460/T));
ct=2
ft=2
To=330
Kc=10*exp(4.8*(432/T-1.5))
k2=k1/Kc
ca=ct*fa/ft*To/T
cb=ct*fb/ft*To/T
r1a=-k1*ca
r3a=-k3*ca
rc=-r3a
r2b=-k2*cb
rb=-r1a+r2b
ra=-r2b-r1a+r3a
w0 = 0.  wf = 100
```

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	100	0	100
fb	1	1.37086	0.48269	0.48269
fa	1	1.23955	0.627195	1.04039
fc	0	0.476925	0	0.476925
T	330	500.098	330	500.098
Ua	16	16	16	16
Ta	500	500	500	500
Dhr1a	-1800	-1800	-1800	-1800
Dhr3a	-1100	-1100	-1100	-1100
cpa	100	100	100	100
cpb	100	100	100	100
cpc	100	100	100	100
k1	0.53124	1.02747	0.53124	1.02747
k3	0.000816537	0.00723019	0.000816537	0.00723019
ct	2	2	2	2
ft	2	2	2	2
To	330	330	330	330
Kc	3.88503	3.88503	0.462911	0.462911
k2	0.13674	2.21959	0.13674	2.21959
ca	1	1	0.566569	0.68652
cb	1	1.25646	0.318513	0.318513
r1a	-0.53124	-0.360779	-0.834834	-0.705382
r3a	-0.000816537	-0.000755951	-0.00565343	-0.00496367
rc	0.000816537	0.00565343	0.000755951	0.00496367
r2b	-0.13674	-0.13674	-0.839884	-0.706969
rb	0.3945	0.3945	-0.0581793	-0.0015878
ra	-0.395316	0.0570191	-0.395316	-0.00137587

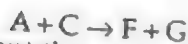
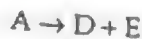
- a) As seen in the above table, the lowest concentration of o-xylene (A) = .57mol/dm³
- b) The maximum concentration of m-xylene (B) = 1.26 mol/dm³
- c) The maximum concentration of o-xylene = 1 mol/dm³
- d) The same equations are used except that F_{B0} = 0. The following table is generated.

P8-29 cont'd

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	100	0	100
z _a	2	2	0.746157	1.03729
z _b	0	1.24923	0	0.481215
z _c	0	0.481477	0	0.481477
T	330	500.102	330	500.102
U _a	16	16	16	16
T _a	500	500	500	500
Dhr _{1a}	-1800	-1300	-1800	-1800
Dhr _{3a}	-1100	-1100	-1100	-1100
cp _a	100	100	100	100
cp _b	100	100	100	100
cp _c	100	100	100	100
k ₁	0.53124	1.02748	0.53124	1.02748
k ₃	0.000816537	0.00723042	0.000816537	0.00723042
ct	2	2	2	2
ft	2	2	2	2
To	330	330	330	330
X _c	3.88503	3.88503	0.462896	0.462896
k ₂	0.13674	2.21969	0.13674	2.21969
ca	2	2	0.642753	0.68447
cb	0	1.08752	0	0.117551
r _{1a}	-1.06248	-0.444729	-1.06248	-0.703282
r _{3a}	-0.00163307	-0.00116466	-0.00565086	-0.00494901
rc	0.00163307	0.00565086	0.00116466	0.00494901
r _{2b}	-0	-0	-0.839501	-0.704864
rb	1.06248	1.06248	-0.0496506	-0.00158212
ra	-1.06411	0.0478847	-1.06411	-0.00336689

The lowest concentration of o-xylene = 0.64 mol/dm³. The highest concentration of m-xylene = 1.09 mol/dm³. The maximum concentration of o-xylene = 2 mol/dm³.

e) Decreasing the heat of reaction of reaction 1 slightly decreases the amount of B formed. Decreasing the heat of reaction of reaction 3 causes more of C to be formed. Increasing the feed temperature causes less of A to react and increases formation of C. Increasing the ambient temperature causes a lot of C to be formed.



We want the exiting flow rates of B, D, and F

P8-30 cont'd

Start with mole balances in PFR:

$$\frac{dF_A}{dV} = r_A \quad \frac{dF_B}{dV} = r_B \quad \frac{dF_C}{dV} = r_C \quad \frac{dF_D}{dV} = r_D$$

$$\frac{dF_E}{dV} = r_E \quad \frac{dF_F}{dV} = r_F \quad \frac{dF_G}{dV} = r_G$$

Rate laws:

$$r_A = -r_{1S} - r_{2B} - r_{3T} \quad r_B = r_{1S}$$

$$r_C = r_{1S} - r_{3T} \quad r_D = r_{2B}$$

$$r_E = r_{2B} \quad r_F = r_{3T}$$

$$r_F = r_{3T}$$

$$r_{1S} = \rho(1-\phi) \exp\left(-0.08539 - \frac{10925}{T}\right) \left(P_A - \frac{P_B P_C}{K}\right)$$

$$r_{2B} = \rho(1-\phi) \exp\left(13.2392 - \frac{25000}{T}\right) P_A$$

$$r_{3T} = \rho(1-\phi) \exp\left(0.2961 - \frac{11000}{T}\right) P_A P_C$$

Stoichiometry:

$$P_A = \frac{F_A}{F_T} P_{T0}$$

$$P_B = \frac{F_B}{F_T} P_{T0}$$

$$P_C = \frac{F_C}{F_T} P_{T0}$$

$$F_T = F_A + F_B + F_C + F_D + F_E + F_F + F_G + F_I$$

$$F_I = \text{steamratio} * .00344$$

Energy balance:

$$\frac{dT}{dV} = \frac{-(r_{1S} * \Delta H_{R1A} + r_{2B} * \Delta H_{R2A} + r_{3T} * \Delta H_{R3A})}{F_A * 299 + F_B * 273 + F_C * 30 + F_D * 201 + F_E * 90 + F_F * 249 + F_G * 68 + F_I * 40}$$

Evaluate the parameters:

$$\Delta H_{R1A} = 118,000$$

$$\Delta H_{R2A} = 105,200$$

$$\Delta H_{R3A} = -53,900$$

P8-30 cont'd

$$K_{p1} = \exp(b_1 + \frac{b_2}{T} + b_3 \ln(T) + [(b_4 T + b_5)T + b_6]T)$$

a) Now plugging into POLYMATH with a initial temperature of 800 K we get the following program and answer.

$$F_B = 0.000898 \text{ kmol/s} \quad F_D = 1.07 \cdot 10^{-5} \text{ kmol/s} \quad F_F = 3.59 \cdot 10^{-5} \text{ kmol/s}$$

8-30

Equations:

	<u>Initial value</u>
d(fa)/d(v)=ra	0.00344
d(fb)/d(v)=rb	0
d(fc)/d(v)=rc	0
d(fd)/d(v)=rd	0
d(fe)/d(v)=re	0
d(ff)/d(v)=rf	0
d(fg)/d(v)=rg	0
d(T)/d(v) = -(r1s*H1a+r2b*H2a+r3t*H3a)/(fa*299+fb*273+fc*300+fd*201+fe*90+ff*68+fi*40)	800

$$H1a=118000$$

$$H2a=105200$$

$$H3a=-53900$$

$$p=2137$$

$$\phi=0.4$$

$$K1=\exp(-17.34-1.302e4/T+5.051\ln(T)+((-2.314e-10\cdot T+1.302e-6)\cdot T-4.931e-3)\cdot T)$$

$$sr=14.5$$

$$fi=sr\cdot 0.00344$$

$$ft=fa+fb+fc+fd+fe+ff+fg+fi$$

$$Pa=fa/ft\cdot 2.4$$

$$Pb=fb/ft\cdot 2.4$$

$$Pc=fc/ft\cdot 2.4$$

$$r1b=p\cdot (1-\phi)\cdot \exp(13.2392-25000/T)\cdot Pa$$

$$r2=r2b$$

$$r3=r2b$$

$$r3t=p\cdot (1-\phi)\cdot \exp(.2961-11000/T)\cdot Pa\cdot Pc$$

$$r7=r3t$$

$$r8=r3t$$

$$r1s=p\cdot (1-\phi)\cdot \exp(-.08539-10925/T)\cdot (Pa-Pb\cdot Pc/K1)$$

$$r2=r1s$$

$$r2=r1s-r3t$$

$$r2b=r1s-r2b-r3t$$

$$v_0 = 0, \quad v_f = 10$$

8-30

<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
v	0	10	0	10
fa	0.00344	0.00344	0.00249597	0.00249597
fb	0	0.000897375	0	0.000897375
fc	0	0.000861498	0	0.000861498
fd	0	1.07785e-05	0	1.07785e-05
fe	0	1.07785e-05	0	1.07785e-05
ff	0	3.58772e-05	0	3.58772e-05
fg	0	3.58772e-05	0	3.58772e-05
T	800	800	765.237	765.237
H1a	118000	118000	118000	118000
H2a	105200	105200	105200	105200
H3a	-53900	-53900	-53900	-53900
p	2137	2137	2137	2137
phi	0.4	0.4	0.4	0.4
K1	0.0459123	0.0459123	0.0196554	0.0196554
sr	14.5	14.5	14.5	14.5
fi	0.04988	0.04988	0.04988	0.04988
ft	0.05332	0.0542282	0.05332	0.0542282
Pa	0.154839	0.154839	0.110465	0.110465
Pb	0	0.0397155	0	0.0397155
Pc	0	0.0381277	0	0.0381277
r2b	2.99119e-06	2.99119e-06	5.16009e-07	5.16009e-07
rd	2.99119e-06	2.99119e-06	5.16009e-07	5.16009e-07
re	2.99119e-06	2.99119e-06	5.16009e-07	5.16009e-07
r3t	0	4.19563e-06	0	4.15139e-06
rf	0	4.19563e-06	0	4.15139e-06
rg	0	4.19563e-06	0	4.15139e-06
r1s	0.000213755	0.000213755	2.48131e-05	2.48131e-05
rb	0.000213755	0.000213755	2.48131e-05	2.48131e-05
rc	0.000213755	0.000213755	2.06617e-05	2.06617e-05
ra	-0.000216746	-2.94805e-05	-0.000216746	-2.94805e-05

P8-30 cont'd

b) $T_0 = 930 \text{ K}$

$F_B = 0.00194 \text{ kmol/s}$

$F_D = 0.000217 \text{ kmol/s}$ $F_F = 0.000204 \text{ kmol/s}$

8-30

Variable	Initial value	Maximum value	Minimum value	Final value
v	0	10	0	10
fa	0.00344	0.00344	0.00108529	0.00108529
fb	0	0.00193494	0	0.00193494
fc	0	0.00174035	0	0.00173155
fd	0	0.000216382	0	0.000216382
fe	0	0.000216382	0	0.000216382
ff	0	0.000203387	0	0.000203387
fg	0	0.000203387	0	0.000203387
T	930	930	850.383	850.383
H1a	118000	118000	118000	118000
H2a	105200	105200	105200	105200
H3a	-53900	-53900	-53900	-53900
p	2137	2137	2137	2137
phi	0.4	0.4	0.4	0.4
K1	0.630438	0.630438	0.13914	0.13914
sr	14.5	14.5	14.5	14.5
fi	0.04988	0.04988	0.04988	0.04988
ft	0.05332	0.0554713	0.05332	0.0554713
Pa	0.154839	0.154839	0.0469559	0.0469559
Pb	0	0.0837162	0	0.0837162
Pc	0	0.0753373	0	0.0749166
r2b	0.000236028	0.000236028	5.77759e-06	5.77759e-06
rd	0.000236028	0.000236028	5.77759e-06	5.77759e-06
re	0.000236028	0.000236028	5.77759e-06	5.77759e-06
r3t	0	3.10453e-05	0	1.46241e-05
rf	0	3.10453e-05	0	1.46241e-05
rg	0	3.10453e-05	0	1.46241e-05
rls	0.00144198	0.00144198	5.83176e-06	5.83176e-06
rb	0.00144198	0.00144198	5.83176e-06	5.83176e-06
rc	0.00144198	0.00144198	-8.79236e-06	-8.79236e-06
ra	-0.001678	-2.62335e-05	-0.001678	-2.62335e-05

c) $T_0 = 1100 \text{ K}$

$F_B = 0.00165 \text{ kmol/s}$

$F_D = 0.00161 \text{ kmol/s}$ $F_F = 0.000127 \text{ kmol/s}$

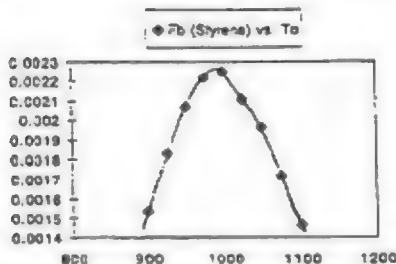
8-30

Variable	Initial value	Maximum value	Minimum value	Final value
v	0	10	0	10
fa	0.00344	0.00344	5.15006e-05	5.15006e-05
fb	0	0.00174939	0	0.0016543
fc	0	0.00164874	0	0.00152682
fd	0	0.00160673	0	0.00160673
fe	0	0.00160673	0	0.00160673
ff	0	0.00012747	0	0.00012747
fg	0	0.00012747	0	0.00012747

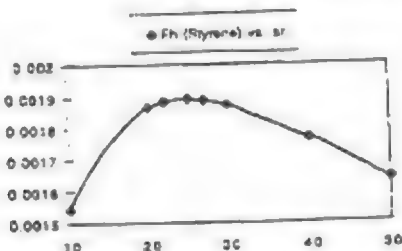
P8-30 cont'd

T	1100	1100	980.458	981.412
H1a	118000	118000	118000	118000
H2a	105200	105200	105200	105200
H3a	-53900	-53900	-53900	-53900
P	2137	2137	2137	2137
phi	0.4	0.4	0.4	0.4
K1	7.68635	7.68635	1.44882	1.47059
sr	14.5	14.5	14.5	14.5
fi	0.04988	0.04988	0.04988	0.04988
ft	0.05332	0.0565888	0.05332	0.056581
Pa	0.154839	0.154839	0.00218451	0.00218451
Pb	0	0.0742133	0	0.0701703
Pc	0	0.0699522	0	0.0647634
r2b	0.015039	0.015039	1.3615e-05	1.3615e-05
rd	0.015039	0.015039	1.3615e-05	1.3615e-05
re	0.015039	0.015039	1.3615e-05	1.3615e-05
r3t	0	0.000115069	0	3.30759e-06
rf	0	0.000115069	0	3.30759e-06
zg	0	0.000115069	0	3.30759e-06
rls	0.00885966	0.00885966	-1.63841e-05	-1.56075e-05
rb	0.00885966	0.00885966	-1.63841e-05	-1.56075e-05
rc	0.00885966	0.00885966	-2.01381e-05	-1.8915e-05
ra	-0.0238986	-1.3151e-06	-0.0238986	-1.3151e-06

d) Plotting the production of styrene as a function of T_0 gives the following graph. The temperature that is ideal is 995K



e) Plotting the production of styrene as a function of the steam ratio gives the following graph and the ratio that is the ideal is 25:1.



f) No solution will be given

g) No solution will be given.

Mole balances

$$V = \frac{v_0(C_{A0} - C_A)}{-r_A}$$

$$V = \frac{v_0(C_{B0} - C_B)}{-r_B}$$

$$V = \frac{v_0 C_D}{r_D}$$

$$V = \frac{v_0 C_U}{r_U}$$

Rate laws:

$$-r_A = k_1 C_A + k_2 C_B \quad r_D = k_1 C_A$$

$$-r_B = k_1 C_A + k_2 C_B \quad r_U = k_2 C_B$$

Energy balance:

$$-F_{A0}[C_{pA}(T - T_{A0}) + C_{pB}(T - T_{B0})] + V(r_{A1})(\Delta H_{R1}(T_R) + \Delta C_{p1}(T - T_R)) + V(r_{A2})(\Delta H_{R2}(T_R) + \Delta C_{p2}(T - T_R))$$

Evaluating the parameters:

$$T = 400K$$

$$k_1 = 1000 \exp\left(-\frac{2000}{T}\right) = 6.73 \quad k_2 = 2000 \exp\left(-\frac{3000}{T}\right) = 1.11$$

$$\Delta C_{p1} = 50 - 20 - 30 = 0 \quad \Delta C_{p2} = 40 - 30 - 20 = -10$$

$$v_0 = \frac{F_{A0}}{C_{A0}} = \frac{60}{.01} = 6000 \frac{\text{dm}^3}{\text{min}} \quad C_{B0} = C_{A0}$$

Simplifying:

$$C_A = \tau * r_A + C_{A0} \quad C_B = \tau * r_B + C_{B0}$$

$$C_D = \tau * r_D \quad C_U = \tau * r_U$$

$$V = \frac{171000}{20190 * C_A + 6660 * C_B}$$

We can plug those into POLYMATH and find the exit concentrations of U and D and find the volume of the CSTR.

Equations:

$$f(ca) = \tau * ra + cao - ca$$

$$f(cb) = \tau * rb + cbo - cb$$

$$f(cd) = cd - \tau * rd$$

$$f(cu) = cu - \tau * ru$$

$$f(V) = 171000 / (20190 * ca + 6660 * cb) - V$$

$$cao = .01$$

$$cbo = .01$$

$$vo = 6000$$

$$k1 = 6.73$$

$$k2 = 1.11$$

$$\tau = V / vo$$

$$rd = k1 * ca$$

$$ru = k2 * cb$$

$$ra = -k1 * ca - k2 * ca$$

$$rb = ra$$

Initial value

$$0.0017$$

$$0.0017$$

$$0.0072$$

$$0.0012$$

$$3794$$

P8-31 cont'd

Variable	8-31	
	Solution	
Variable	Value	f()
ca	0.00167821	-3.12e-18
cb	0.00167821	-3.12e-18
cd	0.00714358	-2.158e-18
cu	0.00117821	-3.686e-19
U	3794.94	-8.531e-13
cao	0.01	
cbo	0.01	
vo	6000	
k1	6.73	
k2	1.11	
tau	0.63249	
rd	0.0112944	
ru	0.00186282	
ra	-0.0131572	
rb	-0.0131572	

a) $C_u = .0012$
 $C_b = .0072$

b) $V = 3794 \text{ dm}^3$

c) No solution will be given.

Mole balances:

$$V = \frac{(C_{A0} - C_A)v_0}{-r_A}$$

$$V = \frac{v_0 C_B}{r_B}$$

This solution only uses one CSTR, if there is more than one CSTR, then the mole balances would both look like the first one.

Rate law:

$$-r_A = k_1 C_A$$

$$r_B = k_1 C_A - k_2 C_B$$

Energy balance:

$$T = \frac{100f(T_a) + F_{A0}C_{pA}T_0 + (-\Delta H_{rx1})(-r_A V) + (-\Delta H_{rx2})(-r_B V)}{100f + F_{A0}C_{pA}}$$

Evaluate the parameters:

$$k_1 = 0.3 \exp \left[7000 \left(\frac{1}{300} - \frac{1}{T} \right) \right]$$

$$k_2 = 0.03 \exp \left[7000 \left(\frac{1}{300} - \frac{1}{T} \right) \right]$$

POLYMATH

8-32

Equations:

$$f(ca) = ca - ca_0 - \tau a \cdot r_a$$

$$f(cb) = cb - \tau a \cdot r_b$$

$$f(T) = (100 \cdot f \cdot T_a + f_{a0} \cdot c_{pA} \cdot T_0 + V \cdot (Dhr1 \cdot r_a + Dhr2 \cdot r_b)) / (100 \cdot f + f_{a0} \cdot c_{pA}) - T$$

$$ca_0 = 5$$

$$\tau a = 6$$

$$f = 0$$

$$T_a = 273$$

$$c_{pA} = 20$$

$$T_0 = 273$$

$$V = 4$$

$$Dhr1 = 10000$$

$$Dhr2 = -10000$$

$$k1 = .3 \cdot \exp(7000 \cdot (1/300 - 1/T))$$

$$k2 = .03 \cdot \exp(7000 \cdot (1/300 - 1/T))$$

$$r_a = -k1 \cdot ca$$

$$r_b = k1 \cdot ca - k2 \cdot cb$$

$$v_0 = V / \tau a$$

$$f_{a0} = ca_0 \cdot v_0$$

Initial value

2

2

100

8-88

Variable	8-32 Solution	
	Value	f()
ca	4.89538	2.971e-13
cb	0.104393	-2.962e-13
T	252.099	-5.929e-11
cao	5	
tau	6	
f	0	
Ta	273	
cpa	20	
To	273	
V	4	
Dhr 1	10000	
Dhr 2	~10000	
k1	0.00356174	
k2	0.000356174	
ra	-0.0174361	
rb	0.0173989	
vo	0.666667	
fao	3.33333	

From POLYMATH we see that we get a $C_B = 0.104 \text{ mol/dm}^3$ and a $v_0 = 0.67 \text{ dm}^3/\text{min}$. This gives us a $F_B = .06968 \text{ mol/min}$ which is also 100 mol/day . The parameters that work for this are as follows:

$$\begin{aligned}
 T_0 &= 273\text{K} \\
 v_0 &= 0.67 \text{ dm}^3/\text{min} \\
 V &= 4 \text{ dm}^3 \\
 f &= 0 \\
 C_{A0} &= 0
 \end{aligned}$$

a) The first task is to find the equilibrium conversion. We need to use the following equations:

$$K_c = \frac{C_B^2}{C_A} = \frac{\frac{4C_{A0}^2 X_e^2 \left(\frac{T_0}{T}\right)^2}{(1 + \epsilon X_e)^2}}{\frac{C_{A0}(1 - X_e)}{(1 + \epsilon X_e)}}$$

$$X_e^2(\epsilon K_c T + 4C_{A0}T_0) - \epsilon TK_c X_e - TK_c = 0$$

$$X_e = \frac{\epsilon TK_c - \sqrt{(\epsilon TK_c)^2 - 4(\epsilon K_c T + 4C_{A0}T_0)TK_c}}{2(\epsilon K_c T + 4C_{A0}T_0)}$$

$$X_{eb} = \frac{C_{pA}(T - T_0) + 0.2 * C_{pI}(T - T_0)}{-\Delta H_{rx} - \Delta C_p(T - T_R)}$$

Then K changes with temperature so we need to come up with that equation:

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H_{rx} + \Delta C_p(T - T_R)}{RT^2}$$

$$\ln K_c = \ln K_p - \ln T - \ln R$$

POLYMATH

8-A1

Equations:

$$d(\ln k_p)/dT = (Dh_{rx1} + Dcp * (T - Tr)) / (R * T^2)$$

$$cao = .5$$

$$Dh_{rx1} = -75000$$

$$Dcp = 8$$

$$Tr = 300$$

$$R = 8.314$$

$$cpa = 12$$

$$To = 300$$

$$cpi = 15$$

$$\epsilon ps = .8$$

$$kc = \exp(\ln kp - \ln(T) - \ln(R))$$

$$Xe = (eps * T * kc + \sqrt{4 * (eps * kc * T + 4 * cao * To) * T * kc}) / (2 * (eps * kc * T + 4 * cao * To))$$

$$xeb = (cpa * (T - To) + .2 * cpi * (T - To)) / (-Dh_{rx1} - Dcp * (T - Tr))$$

$$T_0 = 300, \quad T_f = 542.3$$

Initial value

18.98

8-A1

Variable	Initial value	Maximum value	Minimum value	Final value
T	300	642.3	300	642.3
lnkp	18.98	18.98	3.17469	3.17469
cao	0.5	0.5	0.5	0.5
Dhrxi	-75000	-75000	-75000	-75000
Dcp	8	8	8	8
Tr	300	300	300	300
R	8.314	8.314	8.314	8.314
cpa	12	12	12	12
To	300	300	300	300
cpi	15	15	15	15
eps	0.8	0.8	0.8	0.8
kc	70142	70142	0.0044792	0.0044792
Xe	1.618	1.618	0.0710356	0.0710356
xeb	0	0.0710543	0	0.0710543

We find that the equilibrium conversion is 0.071

$$X = 0.0568$$

To find the volume necessary we can then use the algorithm starting with the mole balance:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

Rate law:

$$-r_A = k \left(C_A - \frac{C_B^2}{K_c} \right)$$

Stoichiometry:

$$C_A = \frac{C_{A0}(1-X) T_0}{1+\epsilon X T} \quad C_B = \frac{2C_{A0}X T_0}{1+\epsilon X T}$$

Energy balance:

$$T = \frac{X[-\Delta H_{rx}^\circ + \Delta C_p T_R] + C_{pA} T_0 + \theta_I C_{pI} T_0}{C_{pA} + \theta_I C_{pI} + X \Delta C_p}$$

Evaluate the parameters:

$$\ln \frac{0.217}{0.324} = \frac{E}{R} \left(\frac{1}{340} - \frac{1}{300} \right)$$

8-91

CDP8-A cont'd

$$\frac{E}{R} = 1022.16$$

$$k = 0.217 \cdot \exp \left[1022.16 \left(\frac{1}{300} - \frac{1}{T} \right) \right]$$

$$\Delta C_p = 2C_{pB} - C_{pA} = 8 \text{ J/molK}$$

$$\frac{d \ln K_p}{dT} = \frac{\Delta H_{rx} + \Delta C_p (T - T_R)}{RT^2}$$

$$\int_{K_{pR}}^{K_{p2}} d \ln K_p = \int_{T_R}^T \frac{\Delta H_{rx} + \Delta C_p (T - T_R)}{RT^2} dT$$

$$\ln \frac{K_{p2}}{K_{pR}} = - \left[\frac{\Delta H_{rx} - \Delta C_p (T_R)}{R} \right] \left[\frac{1}{T} - \frac{1}{T_R} \right] + \frac{\Delta C_p}{R} \ln \frac{T}{T_R}$$

$$\text{But } K_p = \frac{P_B^2}{P_A} = \frac{C_B^2 (RT)^2}{C_A (RT)} = K_C RT \Rightarrow \ln K_p = \ln K_C + \ln T + \ln R$$

$$\therefore \ln \left(\frac{K_{C2}}{K_{CR}} \right) = \frac{\ln K_{p2}}{\ln K_{pR}} - \ln \frac{T}{T_R} = - \left[\frac{\Delta H_{rx} - \Delta C_p T_R}{R} \right] \left[\frac{1}{T} - \frac{1}{300} \right] + \left[\frac{8}{8.314} - 1 \right] \ln \frac{T}{300}$$

$$\ln \left(\frac{K_{C2}}{70000} \right) = - \left[\frac{-75000 - 8 \cdot 300}{8.314} \right] \left[\frac{1}{T} - \frac{1}{300} \right] + \left[\frac{8}{8.314} - 1 \right] \ln \frac{T}{300}$$

$$K_{C2} = 70000 \exp \left[9309.6 \left(\frac{T_R - T}{T_R T} \right) - 0.0378 \ln \frac{T}{T_R} \right]$$

POLYMATH

8-A(a)

Equations:

d(v)/d(x)=fao/-ra

vo=100

cao=.5

eps=.8

To=300

Tr=300

Dhrx1=-75000

cpa=12

cpi=15

cpb=10

l=v/(3.1416*.25^2)

x1=600*x

fao=vo*cao

Dcp=2*cpb-cpa

T=(x*(-Dhrx1-x*Dcp*Tr)+cpa*To+.2*cpi*To)/(cpa+.2*cpi-x*Dc

p)

Initial value

0

CDP8-A cont'd

$$k = 0.217 \cdot \exp(1022.16 \cdot (1/300 - 1/T))$$

$$K_c = 70000 \cdot \exp(9309.6 \cdot (T_r - T) / (T_r \cdot T)) - 0.0378 \cdot 2n(T/T_r)$$

$$c_a = (c_{ao} \cdot (1-x) \cdot T_o) / ((1+\epsilon \cdot x) \cdot T)$$

$$c_b = (2 \cdot c_{ao} \cdot x \cdot T_o) / ((1+\epsilon \cdot x) \cdot T)$$

$$r_a = -k \cdot (c_a - c_b \cdot 2 / K_c)$$

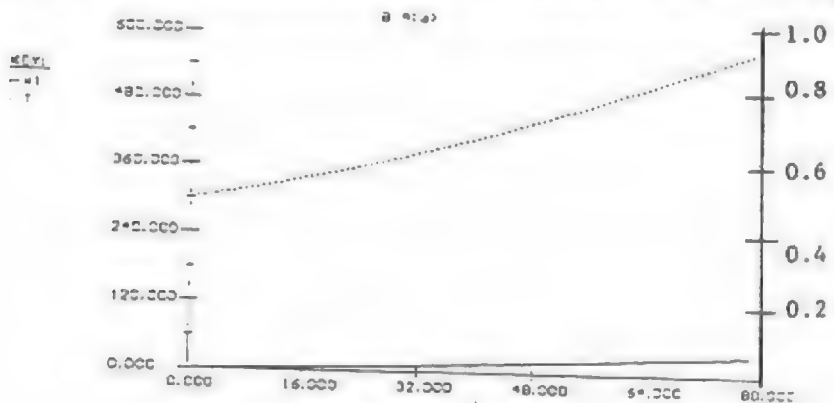
$$x_0 = 0, \quad x_f = 0.057$$

8-A(a)

Variable	Initial value	Maximum value	Minimum value	Final value
x	0	0.057	0	0.057
v	0	15.4136	0	15.4136
v _o	100	100	100	100
c _{ao}	0.5	0.5	0.5	0.5
ε	0.8	0.8	0.8	0.8
T _o	300	300	300	300
T _r	300	300	300	300
Dh _{rxl}	-75000	-75000	-75000	-75000
c _{pa}	12	12	12	12
c _{pi}	15	15	15	15
c _{pb}	10	10	10	10
l	0	78.5007	0	78.5007
x _l	0	34.2	0	34.2
f _{ao}	50	50	50	50
D _{cp}	8	8	8	8
T	300	568.245	300	568.245
k	0.217	1.08387	0.217	1.08387
K _c	70000	70000	0.0296935	0.0296935
c _a	0.5	0.5	0.238068	0.238068
c _b	0	0.0287803	0	0.0287803
r _a	-0.1085	-0.1085	-0.239856	-0.227801

We find that the volume necessary is 15.4 dm³.

b) This graph shows conversion and temperature as a function of length.



CDP8-A cont'd

c) In a CSTR all that will change is the mole balance:

$$V = \frac{F_{A0}X}{-r_A}$$

POLYMATH

8-A(c)

Equations:

$$f(V) = f_{A0}X / -r_A - V$$

$$X = .06$$

$$T_0 = 300$$

$$c_{A0} = .5$$

$$v_0 = 100$$

$$\epsilon = .8$$

$$T_r = 300$$

$$D_{hrx} = -75000$$

$$c_{pi} = 15$$

$$c_{pa} = 12$$

$$c_{pb} = 10$$

$$f_{A0} = c_{A0} \cdot v_0$$

$$D_{cp} = 2 \cdot c_{pb} - c_{pa}$$

$$T = [X \cdot (-D_{hrx} + D_{cp} \cdot T_r) + .2 \cdot c_{pi} \cdot T_0 + c_{pa} \cdot T_0] / (c_{pa} + .2 \cdot c_{pi} \cdot X \cdot D_{cp})$$

$$K = .217 \cdot \exp(1022.16 \cdot (1/300 - 1/T))$$

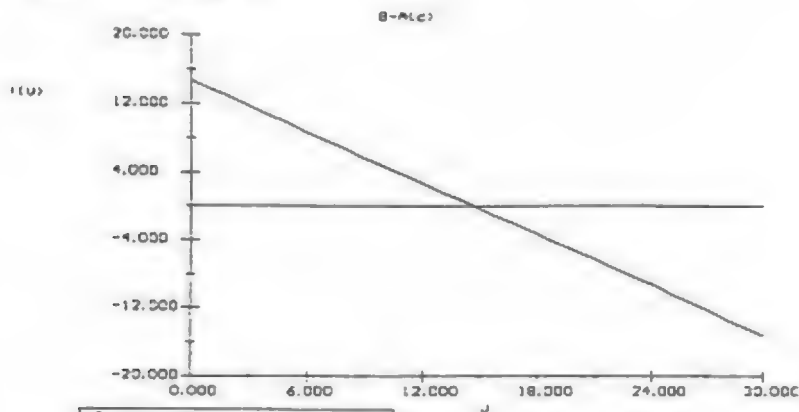
$$K_c = 70000 \cdot \exp(9306 \cdot (T_r - T) / (T_r \cdot T) - .0378 \cdot \ln(T/T_r))$$

$$c_a = c_{A0} \cdot (1 - X) \cdot T_0 / ((1 + \epsilon \cdot X) \cdot T)$$

$$c_b = 2 \cdot c_{A0} \cdot X \cdot T_0 / ((1 + \epsilon \cdot X) \cdot T)$$

$$r_A = -K \cdot (c_a - c_b^2 / K_c)$$

$$V_{min} = 0, \quad V_{max} = 30$$



CDP8-A cont'd

We find that the volume necessary is 14.8 dm³.

d) The only thing that changes is the energy balance from part (a):

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)(-\Delta H_R - \Delta C_p(T - T_R))}{F_{A0}(C_{pA} + 0.2C_{pI} + X\Delta C_p)}$$

$$a = \frac{2\pi r l}{\pi r^2 l} = \frac{2}{r} = \frac{2}{.25} = 8$$

POLYMATH gives us the following graphs.

8-A(d)

Equations:

Initial value

$$d(T)/d(v) = (U \cdot a \cdot (T_a - T) + (-r_A) \cdot (-\Delta H_R - \Delta C_p \cdot (T - T_R))) / (f_{A0} \cdot (c_{pA} + 0.2 \cdot c_{pI} + X \cdot \Delta C_p))$$

300

$$d(X)/d(v) = -r_A / f_{A0}$$

0

$$k = .217 \cdot \exp(1022.16 \cdot (1/300 - 1/T))$$

$$U = 10$$

$$a = 8$$

$$T_a = 300$$

$$\Delta H_R = -75000$$

$$\Delta C_p = 8$$

$$T_R = 300$$

$$c_{pA} = 12$$

$$c_{pI} = 15$$

$$v_0 = 100$$

$$c_{A0} = .5$$

$$\epsilon = .8$$

$$T_0 = 300$$

$$x_1 = x \cdot 600$$

$$l = v / (3.1416 \cdot .25^2)$$

$$K_c = 70000 \cdot \exp(9309.6 \cdot (T_R - T) / (T_R \cdot T) - .0378 \cdot \ln(T / T_R))$$

$$f_{A0} = c_{A0} \cdot v_0$$

$$c_A = c_{A0} \cdot (1 - X) \cdot T / ((1 - \epsilon \cdot X) \cdot T_0)$$

$$c_B = 2 \cdot c_{A0} \cdot X \cdot T / ((1 - \epsilon \cdot X) \cdot T_0)$$

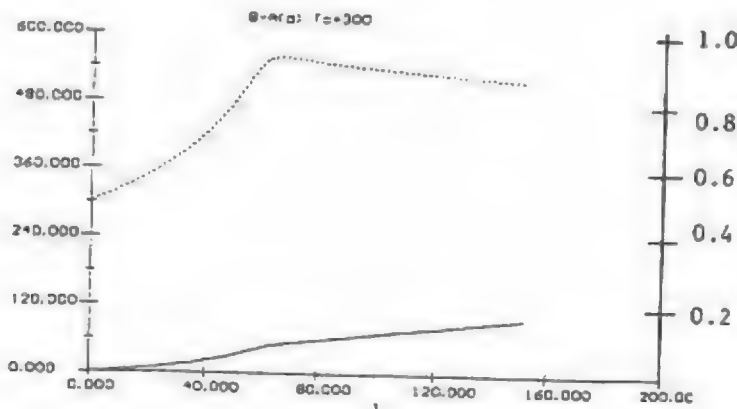
$$r_A = -k \cdot (c_A - c_B^2 / K_c)$$

$$v_0 = 0, \quad v_f = 30$$

KEY:

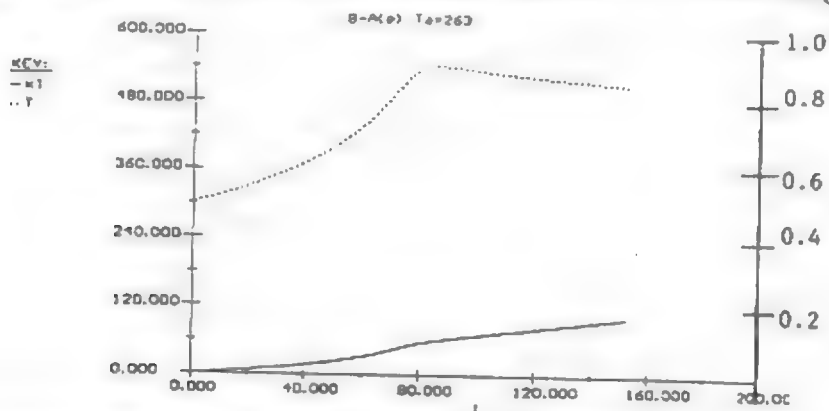
--x1

--T

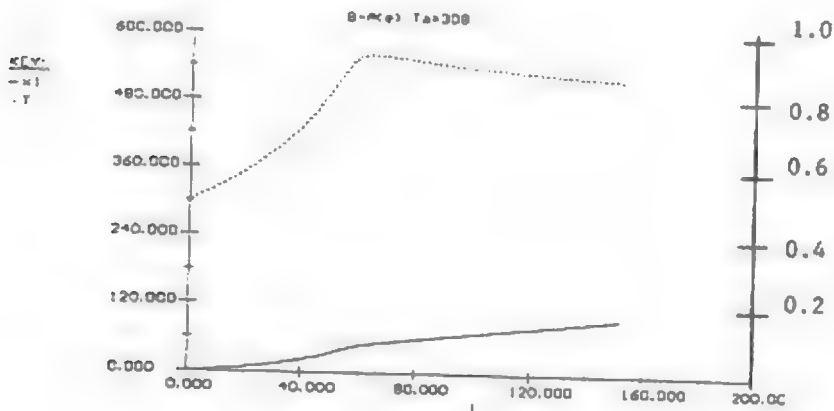


8-95

e) For winter operation assume a temperature of -10°C . This is the graph:



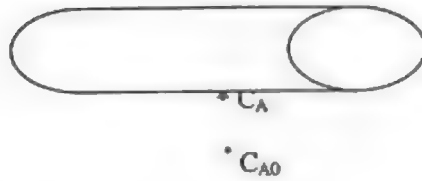
For summer operation assume a temperature of 35°C This is the graph.



CDP8-B

A \rightarrow products

$$-r_A'' = \frac{k_1 C_A}{(k_2 + k_3 C_A)^2} \frac{\text{gmol}}{\text{cm}^2 \text{s}}$$



a)

$$Sh = \frac{k_L D}{D_{AB}} = 0.4 Re^{0.4} Sc^{1/3} = 0.4 Re^{0.4} Sc^{1/3}$$

Convective diffusive flux

$$J_D = k_L (C_{A0} - C_A) = \frac{Sh D_{AB}}{D} (C_{A0} - C_A)$$

Reaction Rate/Area

$$J_R = -r_A'' = \frac{k_1 C_A}{(k_2 + k_3 C_A)^2}$$

At steady state:

$$J_D = J_R$$

$$\frac{Sh D_{AB}}{D} (C_{A0} - C_A) = \frac{k_1 C_A}{(k_2 + k_3 C_A)^2} \quad (1)$$

At Bifurcation point,

$$\left. \frac{\partial J_D}{\partial C_A} \right|_{C_A^*} = \left. \frac{\partial J_R}{\partial C_A} \right|_{C_A^*}$$

$$-\frac{Sh D_{AB}}{D} = \frac{k_1}{(k_2 + k_3 C_A^*)^2} \left[1 - \frac{2 C_A^* k_3}{k_2 + k_3 C_A^*} \right] \quad (\alpha)$$

$$-\frac{Sh D_{AB}}{D} = \frac{k_1 (k_2 - k_3 C_A^*)}{(k_2 + k_3 C_A^*)^3}$$

$$\frac{k_1 C_A^*}{(k_2 + k_3 C_A^*)^2} = -\frac{ShD_{AB}}{D} \left(\frac{k_2 + k_3 C_A^*}{k_2 - k_3 C_A^*} \right) C_A^*$$

Substituting this in (1), at steady state:

$$\begin{aligned} \frac{ShD_{AB}}{D} (C_{A0} - C_A^*) &= -\frac{ShD_{AB}}{D} \left(\frac{k_2 + k_3 C_A^*}{k_2 - k_3 C_A^*} \right) C_A^* \\ (C_{A0} - C_A^*)(k_2 - k_3 C_A^*) &= -(k_2 + k_3 C_A^*) C_A^* \\ k_2 C_{A0} - (k_2 + k_3 C_{A0}) C_A^* + k_3 C_A^{*2} &= -k_2 C_A^* - k_3 C_A^{*2} \\ 2k_3 C_A^{*2} - k_3 C_{A0} C_A^* + k_2 C_{A0} &= 0 \end{aligned} \quad (2)$$

For equation (2) having real solution:

$$\begin{aligned} (-k_3 C_{A0})^2 - 4 * 2k_3 * k_2 C_{A0} &\geq 0 \\ k_3^2 C_{A0}^2 - 8(k_3 C_{A0}) k_2 &\geq 0 \\ k_3 C_{A0} (k_3 C_{A0} - 8k_2) &\geq 0 \end{aligned}$$

As $k_3 C_{A0} > 0$

$$C_{A0} > \frac{8k_2}{k_3} \quad \text{Condition for having M.S.S}$$

$$\text{Lowest } C_{A0} = \frac{8k_2}{k_3} = \frac{8 * 2}{2000} = 8 * 10^{-3} \frac{\text{gmol}}{\text{cm}^3}$$

b) At bifurcation point both roots of equation (2) for C^* coincide for this

$$\begin{aligned} C_{A0} &= \frac{8k_2}{k_3} \\ C_A^* &= -\frac{(-k_3 C_{A0})}{2k_3} = \frac{C_{A0}}{2} \end{aligned}$$

Substituting this in equation (1)

$$\frac{ShD_{AB}}{D} \left(C_{A0} - \frac{C_{A0}}{2} \right) = \frac{k_1 C_{A0/2}}{(k_2 + k_3 C_{A0}/2)^2}$$

$$\frac{0.4 Re^{0.4} Sc^{1/3} D_{AB}}{D} = \frac{k_1}{k_2 + k_3 \frac{4k_2}{k_3}}$$

$$\frac{U^{0.4}}{D^{0.6}} = \frac{k_1 \nu^{0.4}}{2k_2 D_{AB} Sc^{1/3}}$$

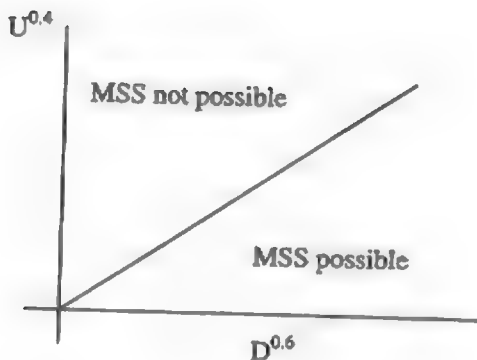
c)

$$\frac{U^{0.4}}{D^{0.6}} = \frac{432(0.1)^{0.4}}{2 * 2 * 0.1 * 1^{1/3}}$$

$$= 430$$

$$U = [430 * 0.025^{0.6}]^{1/0.4}$$

$$= 15152 \frac{cm}{s}$$



I)

$$-r_A = kC_A \quad (1)$$

Plugging that into the CSTR mole balance and writing as a function of C_A .

$$F(C_A) = \frac{C_A}{\tau} - \frac{C_{A0}}{\tau} + kC_A \quad (2)$$

$$F(y) = \alpha C_A - \beta + G(C_A)$$

Taking the derivative of that:

$$\left. \frac{dF}{dC_A} \right|_{C_A^*} = \frac{1}{\tau} + k = 0 \quad (3)$$

There is no point where this is true so this will not have multiple steady-states.

$$\text{II) } -r_A = \frac{kC_A}{1 + KC_A} \quad (4)$$

Plugging that into the CSTR mole balance and writing as a function of C_A :

$$F(C_A) = \frac{C_A}{\tau} - \frac{C_{A0}}{\tau} + \frac{kC_A}{1 + KC_A} \quad (5)$$

Taking the derivative of that:

$$\left. \frac{dF}{dC_A} \right|_{C_A^*} = \frac{1}{\tau} + \frac{k}{(1 + KC_A)^2} = 0 \quad (6)$$

There is no point where this is true so this will not have MSS.

$$\text{III) } -r_A = \frac{kC_A}{(1 + KC_A)^3} \quad (7)$$

Plugging into the CSTR mole balance and writing as a function of C_A :

$$F(C_A) = \frac{C_A}{\tau} - \frac{C_{A0}}{\tau} + \frac{kC_A}{(1 + KC_A)^3} = 0 \quad (8)$$

Taking the derivative of this:

$$\left. \frac{dF}{dC_A} \right|_{C_A^*} = \frac{1}{\tau} + \frac{k - 2kKC_A^*}{(1 + KC_A^*)^4} = 0 \quad (9)$$

Combining the last two equations we come up with:

$$3KC_A^{*2} - 2KC_{A0}C_A^* + C_{A0} = 0 \quad (10) \& (11)$$

$$C_A^* = \frac{2KC_{A0} \pm \sqrt{4KC_{A0}(KC_{A0} - 3)}}{6K}$$

From this we can see that $KC_{A0} > 3$ for this to be true. Next taking equation (9) we find that:

$$\frac{1}{\tau k} = \frac{2KC_A^* - 1}{(1 + KC_A^*)^4} \quad (12)$$

We see that the left side has a maximum so to determine where it is we take the derivative and solve for where it equals zero.

$$\frac{6K - 6K^2C_A^*}{(1 + KC_A^*)^5} = 0 \quad (13)$$

$$C_A^* = \frac{1}{K} \quad (14)$$

Plugging that back into equation (12):

$$\frac{1}{\tau k} = \frac{1}{16} \quad (15)$$

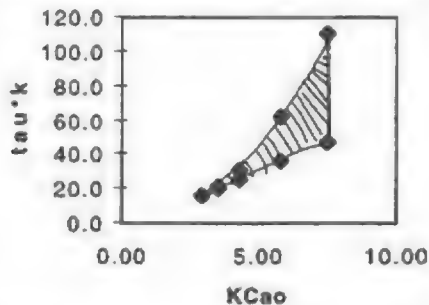
τk cannot be under 16. Now taking $y = C_A/C_{A0}$ and plug into equations (10) and (8) we come up with the following equations:

$$KC_{A0} = \frac{1}{y(2 - 3y)} \quad (16)$$

$$\tau k = \frac{(1 - y)(1 + KC_{A0}y)^3}{y} \quad (17)$$

We can then come up with the following table and graph:

y	KC _{A0}	τk
0.075	7.51	47.1
0.1	5.88	36.1
0.15	4.30	25.2
0.2	3.57	20.2
0.32	3.00	16.0
0.467	3.57	21.7
0.5165	4.30	31.2
0.5666	5.88	62.1
0.5916	7.51	111.2



/// = MSS

CDP8-D

The rate law is:

$$-r_A = \frac{kC_A C_B}{1 + KC_A} \quad (1)$$

Plugging that into the mole balance for a CSTR:

$$F(C_A) = \frac{C_A}{\tau} - \frac{C_{A0}}{\tau} + \frac{kC_A C_B}{1 + KC_A} = 0 \quad (2)$$

For multiple steady-states to occur equation (2) must be true as well as this equation:

CDP8-D cont'd

$$\left. \frac{dF}{dC_A} \right|_{C_A^*} = \frac{1}{\tau} + \frac{kC_B}{(1+KC_A)^2} = 0$$

There is no quantity of C_A where this is true so there are no regions where multiple steady-state occurs.

CDP8-E

Energy balance over system from $Z = 0$ to any Z

$$\dot{Q} - XF_{A0} \left[\Delta H_R^0(T_R) + \int_{T_R}^T \Delta C_p dT \right] = \left[F_{A0} \sum \theta_i \int_{T_i}^T C_{pi} dT \right]$$

Energy balance over system from $Z = 0$ to dZ

$$\begin{aligned} \dot{Q} \cdot \frac{dQ}{dZ} - XF_{A0} \left\{ \Delta H_R^0(T_R) + \int_{T_R}^T \Delta C_p dT \right\} \cdot \frac{d}{dZ} \left\{ XF_{A0} \left[\Delta H_R^0(T_R) + \int_{T_R}^T \Delta C_p dT \right] \right\} \\ = F_{A0} \sum \theta_i \int_{T_i}^{T_R} C_{pi} dT + \frac{d}{dZ} \left[F_{A0} \sum \theta_i \int_{T_i}^{T_R} C_{pi} dT \right] \end{aligned}$$

Subtracting

$$\frac{d\dot{Q}}{dZ} - \frac{d}{dZ} \left[XF_{A0} \left\{ \Delta H_R^0(T_R) + \int_{T_R}^T \Delta C_p dT \right\} \right] = \frac{d}{dZ} \left[F_{A0} \sum \theta_i \int_{T_i}^{T_R} C_{pi} dT \right]$$

$$\text{But } \frac{d}{dZ} \left[F_{A0} \sum \theta_i \int_{T_i}^T C_{pi} dT \right] = F_{A0} \sum \theta_i C_{pi} \frac{dT}{dZ}; \quad \frac{d}{dZ} \int_{T_R}^T \Delta C_p dT = \Delta C_p \frac{dT}{dZ}$$

$$\text{and } \frac{d\dot{Q}}{dZ} = UA(T_A - T)$$

Energy balance becomes:

$$UA(T_A - T) - F_{A0} \left[X \Delta H_R^0(T_R) + \Delta C_p(T - T_R) \right] \frac{dX}{dZ} - XF_{A0} \Delta C_p \frac{dT}{dZ} = F_{A0} \sum \theta_i C_{pi} \frac{dT}{dZ}$$

$$\text{or } \frac{dT}{dZ} = \frac{UA(T - T_A) - F_{A0} \left[X \Delta H_R^0(T_R) + \Delta C_p(T - T_R) \right]}{F_{A0} (\sum \theta_i C_{pi} + X \Delta C_p)} \frac{dX}{dZ}$$

Material balance for $\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3$

$$F_{A0} dX_A = (-r_A) dW, \quad -r_A = k_1 \sqrt{\frac{P_{SO_2}}{P_{SO_2}}} \left[P_{O_2} - \frac{P_{SO_2}^2}{K_p P_{SO_2}^2} \right]$$

$$\text{with } y_{SO_2} = y_A = 0.11, y_{O_2} = 0.1 \text{ and } y_1 = 0.79; \delta = 1 - 1 - \frac{1}{2} = -\frac{1}{2}$$

$$\theta_A = 1.0, \theta_{O_2} = \frac{0.10}{0.11} = 0.91 \text{ and } \theta_1 = \frac{0.79}{0.11} = 7.17; P_0 = 1 \text{ atm}$$

$$P_{SO_2} = C_{SO_2} RT = \frac{RT C_{A0} (1-X)}{1+\varepsilon X} = \frac{P_{A0} (1-X)}{1+\varepsilon X} = \frac{y_{A0} P_0 (1-X)}{1+\varepsilon X}$$

$$P_{O_2} = C_{O_2} RT = C_{A0} RT \left[\frac{\theta_{O_2} - 0.5X}{1+\varepsilon X} \right] = \frac{y_{A0} P_0 (\theta_{O_2} - 0.5X)}{1+\varepsilon X}$$

$$P_{SO_2} = C_{SO_2} RT = \frac{C_{A0} RT X}{1+\varepsilon X} = \frac{y_{A0} P_0 X}{1+\varepsilon X}$$

$$-r_A = k_1 \left[\frac{y_{A0} P_0 (1-X)}{1+\varepsilon X} \right]^{\frac{1}{2}} \left[\frac{y_{A0} P_0 (\theta_{O_2} - 0.5X)}{1+\varepsilon X} - \frac{\left(\frac{y_{A0} P_0 X}{1+\varepsilon X} \right)^2}{K_p \left[\frac{y_{A0} P_0 (1-X)}{1+\varepsilon X} \right]^2} \right]$$

$$-r_A = k_1 \left[\frac{1-X}{X} \right]^{\frac{1}{2}} \left[\frac{y_{A0} P_0 (\theta_{O_2} - 0.5X)}{1+\varepsilon X} - \frac{X^2}{K_p (1-X)^2} \right]$$

$$\text{Now } dW = P_B \frac{\pi D^2}{4} dZ$$

$$\therefore \frac{dX}{dZ} = \frac{-r_A}{F_{A0}} P_B \frac{\pi D^2}{4} = \frac{k_1 P_B \pi D^2}{4 F_{A0}} \left(\frac{1-X}{X} \right)^{\frac{1}{2}} \left[\frac{y_{A0} P_0 (\theta_{O_2} - 0.5X)}{1+\varepsilon X} - \frac{X^2}{K_p (1-X)^2} \right]$$

$$\text{With } P_B = 150 \frac{\text{lb}}{\text{ft}^2}; D = 1 \text{ ft}; \frac{P_B \pi D^2}{4} = \frac{(150)(\pi)(1)}{4} = 117.8 \frac{\text{lb}}{\text{ft}}$$

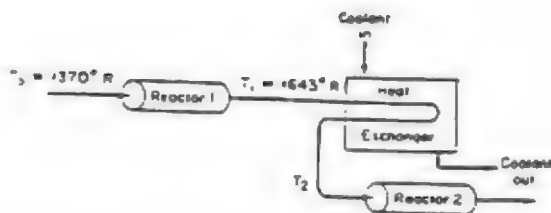
$$\varepsilon = y_{A0} \delta = (0.11)(-0.5) = -0.055; y_{A0} P_0 = 0.11 \text{ atm}$$

$$\begin{aligned} \therefore \frac{dX}{dZ} &= \frac{117.8 k_1}{F_{A0}} \left(\frac{1-X}{X} \right)^{\frac{1}{2}} \left[\frac{0.11(\theta_{O_2} - 0.5X)}{1 - 0.055X} - \frac{X^2}{K_p (1-X)^2} \right] \\ &= \frac{117.8 k_1}{F_{A0}} \left(\frac{1-X}{X} \right)^{\frac{1}{2}} \left[\frac{0.11(0.91 - 0.5X)}{1 - 0.055X} - \frac{X^2}{K_p (1-X)^2} \right] \end{aligned}$$

The equation in the text program calculating the adiabatic temperature has to be replaced by the energy balance. T must now be calculated by a different formula, similar to that for X. If the Euler's method of solving differential equations is used, the expressions of $\frac{dT}{dZ}$ should follow that for $\frac{dX}{dZ}$, since the value of $\frac{dX}{dZ}$ is necessary for its calculation.

After each step, the new value of T may be obtained from the equation.

$$T_{\text{new}} = T_{\text{old}} + \left(\frac{dT}{dZ} \right)_{T_{\text{old}}} \Delta Z$$



Conditions on reactor 1 are fixed; therefore, the outlet conversion, X_{F1} , from the first reactor is determined. This value is used as an entrance condition for reactor 2. The overall conversion can then be maximized in a procedure identical to that outline in problem P-8.

CDP8-G

a) Assuming that there is an unique cost optimum with respect to the inlet temperature T_2 , a routine similar to that outlined in P8-8 and modified as suggested in P8-10(a) can be used. First, the conditional statement cutting off reactor calculations when W exceeds 1000 lb. should be discarded and / or modified such that the reactor calculations cease when X_{F2} exceeds 0.95. Instead of maximizing conversion, a routine similar to that shown in P8-8 minimizing the total cost function can be implemented.

b) This problem appears to be a two-variable optimization. Energy balance can be used to characterize the steam conditions, i.e., $\phi(0, T_0, T_F, X_F) = 0$. By the overall energy balance on system. (Here ϕ is represented in the form

$$T_F = \frac{43.620 X_F + 77.3 T_0}{1.8 X_F + 77.3} = 0,$$

which is an adiabatic energy balance between any T_0 and T_F , given any conversion X_F . Also by an energy balance over the heat exchanger and reactor 2, $\phi(0, T_0, X_1, T_2) = 0$. Since there are three pieces of process equipment, there are three independent energy balances. From this system, the unknowns are: T_F, X_1, T_2, T_0 and T_1 . Therefore, any two of the variables must be set to characterize the system. An optimum subroutine could be devised using a method such as that of the steepest ascent to minimize process costs.

CDP8-H

Find temperature where the concentration of B is the greatest.

$$\tau = \frac{C_{A0} - C_A}{k_1 C_A + k_2 C_A}$$

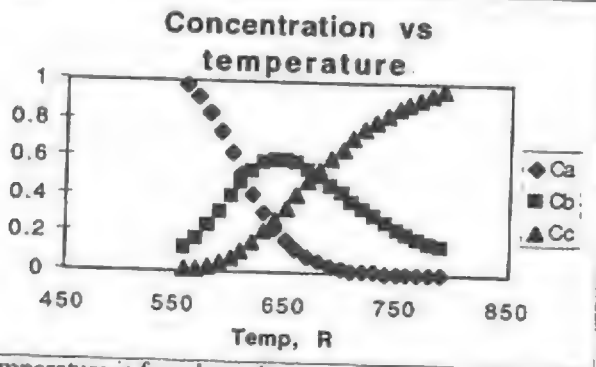
$$\tau = \frac{C_B}{k_1 C_A}$$

$$\tau = \frac{C_C}{k_2 C_A}$$

$$k_1 = 3 \times 10^8 e^{-(27000)/(R \cdot T)}$$

$$k_2 = 2 \times 10^{14} e^{-(45000)/(R \cdot T)}$$

Then graphing those as a function of temperature gives the following graph where the maximum of B occurs at 643°R of 185°F.



Once the temperature is found use the energy balance to determine the area of the heating coil.

$$A = \frac{F_{A0} C_{pA} T_0 + (-\Delta H_{RX1})(-r_{A1} V) + (-\Delta H_{RX2})(-r_{A2} V) - F_{A0} C_{pA} T}{UT - UT_A}$$

$$= \frac{90 \cdot .8 \cdot 130 + 15000 \cdot .199183 \cdot .199868 \cdot 30 - 25000 \cdot .10106 \cdot .199868 \cdot 30 - 90 \cdot .8 \cdot 184}{.111 \cdot 184 - .111 \cdot 212} = 361 \text{ ft}^2$$

CDP8-I

Find the maximum of G(T)

From 8-20

$$X = \frac{\tau k}{1 + \tau k \left(1 + \frac{1}{K}\right)}$$

$$G(T) = (-\Delta H_{RX})X = 80000 \cdot X$$

$$k = e^{-20000 \cdot (1/T - 1/400)}$$

$$K = 100e^{(90000/R \cdot (1/400 - 1/T))}$$

T	k	K	X	G
396	0.6034751	276.40849	0.85519442	68415.5532
398	0.777823	165.831208	0.8813724	70509.7923
400	1	100	0.9009009	72072.0721
402	1.28242936	60.6065371	0.91367851	73094.2808
402.5	1.36418749	53.5164184	0.91575967	73260.7736
403	1.45093538	47.2703356	0.91736725	73389.3801
403.5	1.54296375	41.7660986	0.9184818	73478.5441
404	1.64057945	36.9140939	0.91908048	73526.4385
404.5	1.7441063	32.6357129	0.91913688	73530.9504
405	1.85388595	28.8619781	0.91862084	73489.6672
405.5	1.97027887	25.5323441	0.91749833	73399.8661
406	2.09366529	22.5936505	0.91573134	73258.5069
408	2.66550133	13.8953936	0.90132096	72105.6766
410	3.38553585	8.58647606	0.87260063	69808.0502
412	4.29010273	5.33075524	0.82583193	66066.5542

The maximum X value occurs at 404.5 K and the G value is 73530.

Find where $R(T)$ equals $G(T)$

$$R(T) = C_{pm}(1 + \kappa)(T - T_c)$$

$$T_c = \frac{T_0 + \kappa T_g}{1 + \kappa} = \frac{310 + \kappa * 310}{1 + \kappa} = 310$$

Solving $R(T)$ for κ , $\kappa = 18.45$

$$\kappa = \frac{UA}{F_{A0}C_{pm}}$$

$$UA = 7380$$

CDP8-I

a) Starting with the mole balance in a "fluidized bed"

$$W = \frac{v_0(C_{A0} - C_A)}{-r_A}$$

$$\theta = \frac{W}{v_0}$$

$$\theta = \frac{C_{A0} - C_A}{k_1 C_A}$$

$$\theta = \frac{C_{A0} - C_A}{k_1 C_{A0}(1 - \alpha_p)}$$

$$1 - \alpha_p = \frac{\alpha_p}{k\theta}$$

$$\alpha_p = \frac{k_1 \theta}{1 + k_1 \theta}$$

Using the mole balance on p

$$\theta = \frac{C_p}{k_1 C_A - k_2 C_p}$$

$$C_p = \alpha_p \theta_p C_{A0}$$

$$\theta = \frac{\alpha_p \theta_p C_{A0}}{k_1 C_{A0}(1 - \alpha_p) - \alpha_p \theta_p C_{A0} k_2}$$

$$\theta k_1 C_{A0} - \theta k_1 C_{A0} \alpha_p - \theta \alpha_p \theta_p C_{A0} k_2 = \alpha_p \theta_p C_{A0}$$

$$\theta k_1 - \theta k_1 \alpha_p = \theta \alpha_p \theta_p k_2 + \alpha_p \theta_p$$

$$\theta_p = \frac{\theta k_1 \left(1 - \frac{k_1 \theta}{1 + k_1 \theta} \right)}{\frac{k_1 \theta}{1 + k_1 \theta} (1 + \theta k_2)}$$

Finally:

$$\theta = \frac{C_p}{k_1 C_A - k_2 C_p}$$

$$C_p = C_{A0} \eta$$

$$\theta = \frac{C_{A0} \eta}{k_1 C_{A0}(1 - \alpha_p) - k_2 C_{A0} \eta}$$

$$k_1 \theta (1 - \alpha_p) - k_2 \theta \eta = \eta$$

$$\eta = \frac{k_1 \theta \left(1 - \frac{k_1 \theta}{1 + k_1 \theta} \right)}{1 + k_2 \theta}$$

c) We need equations for the two k's and the equation to find a. Every other quantity or equation is known.

CDP8-J

cont'd

$$k_1 = 5.33 \cdot 10^{15} \cdot \exp\left[\frac{43900}{1.987} \left(\frac{1}{423} - \frac{1}{T}\right)\right]$$

T in K

$$k_2 = 2.65 \cdot 10^5 \cdot \exp\left[\frac{20414}{1.987} \left(\frac{1}{423} - \frac{1}{T}\right)\right]$$

$$a = \frac{\frac{C_{A0}}{\theta} C_{PA}(T - T_0) - (-k_1 C_{A0}(1 - \alpha_P) \cdot -449000) - ((k_1 C_{A0}(1 - \alpha_P) - k_2 C_{A0}\eta) \cdot (-784000))}{U(T_a - T)}$$

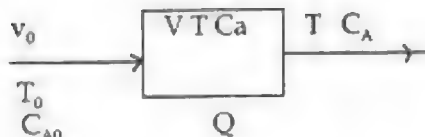
Where T is in °C. We then get this table where with these equations and the temperatures given we find the θ where the concentration of P is maximized.

T	k1	k2	α	η	a	Cp
331	3.3252E+22	383868745	1	0.5714367	1.53251186	0.00025486
365	2.3357E+23	950289557	1	0.35414693	1488.271	0.00015795
423	4.185E+24	3636190933	1	0.11194938	1642.11894	4.9929E-09

θ
1.95E-09

d) No solution will be given.

e) No solution will be given.



Assumed
 $\rho, C_p, \Delta H$ constant

Mole Balance:

$$v_0 C_{A0} - v C_A + \frac{V}{v_0} r_A = \frac{V}{v_0} \frac{dC_A}{dt}$$

$$\text{Let } C_A = C_{A0}(1 - X_A); \quad \tau = \frac{V}{v_0}; \quad r = -\frac{r_A}{C_{A0}}; \quad \theta = \frac{t}{\tau}$$

$$\text{giving } \frac{dX_A}{d\theta} = -X_A + \tau v = F(X_A, T)$$

Rate equation:

$$-r_A = k C_A = k C_{A0}(1 - X_A)$$

$$k = k_{30} \exp\left[-\frac{19870}{1.987} \left(\frac{1}{T} - \frac{1}{303.2}\right)\right]$$

$$r = k(1 - X_A)$$

Energy balance:

$$\dot{Q} - \dot{W}_s + v_0 \rho C_p (T_0 - T) + \Delta H^\circ r_A V = V \rho C_p \frac{dT}{dt} - V \frac{dP}{dt}$$

$$\dot{Q} = 0; \dot{W}_s = 0; \frac{dP}{dt} = 0$$

$$T_0 - T + \frac{\Delta H}{\rho C_p} r_A \frac{V}{v_0} = \frac{V}{v_0} \rho C_p \frac{dT}{dt}$$

$$J = -\frac{\Delta H_r C_{A0}}{\rho C_p}$$

$$\frac{dT}{d\theta} = T_0 - T + \tau J r = G(X_A, T)$$

a) τ for extinction and ignition $C_{A0} = 5 \text{ gmol/dm}^3$

$$J = \frac{(-15120)(5)}{(0.9)(1.21)(1000)} = 70 \text{ K}$$

$$k_{30} = 1.0 \text{ min}^{-1}$$

$$T_0 = 293.2 \text{ K}$$

CDP8-L cont'd

Relations become:

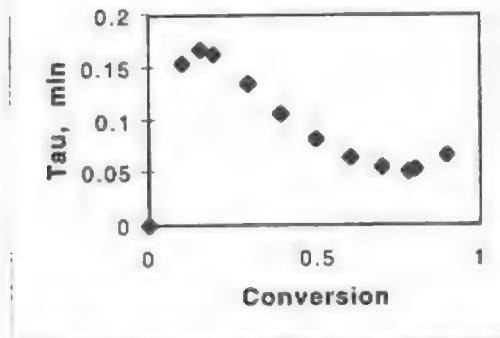
$$-X_A + \tau r = 0$$

$$T_0 - T + \tau J r = 0$$

Energy balance becomes: $T_0 - T + JX_A$

$$\tau = \frac{X_A}{r(X_A, T)} = \frac{X_A}{k_{30}(1 - X_A) \exp \left[-10^4 \left(\frac{1}{T_0 + JX_A} - \frac{1}{303.2} \right) \right]}$$

Tau vs conversion



Could do numerically, but not difficult analytically. IG/ER points are where:

$$\frac{d\tau}{dX_A} = 0$$

$$\ln \tau = \ln X_A - \ln(1 - X_A) + 10^4 \left(\frac{1}{T_0 + JX_A} - \frac{1}{303.2} \right) - \ln k_{30}$$

$$\frac{d}{dX_A} \ln \tau = \frac{1}{X_A} - \frac{1}{1 - X_A} - \frac{10^4 J}{(T_0 + JX_A)^2} = 0$$

$$f(X_A) = \frac{1}{X_A} - \frac{1}{1 - X_A} - \frac{7 \times 10^5}{(293.2 + 70X_A)^2} = 0$$

Roots are: $X_A = 0.1567, 0.7881$

Giving $\tau = 0.16728, 0.05163$

action curve and ignition- $T_0 = 20^\circ\text{C}$, $\tau = 0.1$ min.

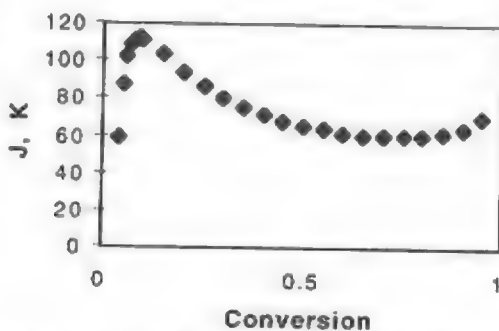
ly in J. Need to find J limits.

$$= \frac{1}{303.2} + 10^{-4} \ln \left(\frac{k_{30} \tau (1 - X_A)}{X_A} \right)$$

$$T_0 + JX_A = \frac{1}{\frac{1}{303.2} + 10^{-4} \ln \left(\frac{k_{30} \tau (1 - X_A)}{X_A} \right)}$$

$$J = \frac{1}{X_A} \left[\frac{303.2}{1 + 0.03032 \ln \left(\frac{k_{30} \tau (1 - X_A)}{X_A} \right)} - T_0 \right]$$

J vs conversion



To find the analytical solution:

$$\frac{d}{dX_A} \ln J = 0$$

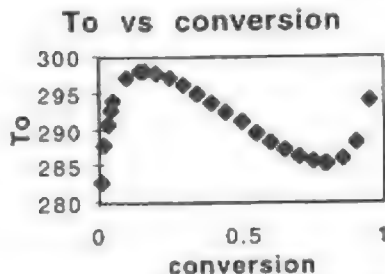
and solve: $X_A = 0.0921, 0.7437$
 $J = 110.01, 59.812 \text{ K}$
 $C_{A0} = 7.8579, 4.2723 \text{ gmol/l}$

c) T_0 for extinction and ignition $\tau = 0.1 \text{ min}$ $C_{A0} = 5$
 Similar procedure. T_0 only enters in energy balance

$$T_0 = \frac{303.2}{\left[1 - 0.03022 \ln \left(\frac{k_{30} \tau (1 - X_A)}{X_A} \right) \right]} - JX_A$$

$$\frac{dT_0}{dX_A} = \frac{303.2(0.03032) \left[\frac{1}{1 - X_A} + \frac{1}{X_A} \right]}{\left[1 - 0.03022 \ln \left(\frac{k_{30} \tau (1 - X_A)}{X_A} \right) \right]^2} - 70 = 0$$

(very similar to J case) in fact, identical! Except that J is fixed and T_0 varies



Roots are: $X_A = 0.1636, 0.7902$

Giving $T_0 = 298.04, 285.37$

[All roots are found with POLYMATH]

2)

a) $F = 0, G = 0$

$$F = 0$$

$$G = 0$$

$$-X_A + \tau r = 0$$

$$T_0 - T + J\tau r = 0$$

$$-X_A + \tau k(1 - X_A) = 0 \quad T_0 - T + \tau jk(1 - X_A) = 0$$

$$X_A = \frac{k\tau}{1 + k\tau}$$

$$X_A = \frac{T_0 - T}{\tau jk} + 1$$

$$k = k_{30} \exp \left[-10^4 \left(\frac{1}{T} - \frac{1}{303.2} \right) \right]$$

Plot attached. Solve simultaneously for X_A and T for $t = 0.1$ min, $k_{30} = 1 \text{ min}^{-1}$, $J = 70 \text{ K}$, and $T_0 = 293.2 \text{ K}$.

Solve above equations simultaneously to find stable and unstable points

$$f(X_A, T) = -X_A + \tau k(1 - X_A) = 0$$

$$g(X_A, T) = T_0 - T + \tau jk(1 - X_A) = 0$$

Use POLYMATH to find the roots of the equations.

Equations:

$$f(x) = -x - \tau \cdot k \cdot (1-x)$$

$$f(T) = T_0 - T + \tau \cdot J \cdot k \cdot (1-x)$$

$$\tau = 0.1$$

$$k = 1 \cdot \exp(-1e4 \cdot (1/T - 1/303.2))$$

$$T_0 = 293$$

$$J = 70$$

Initial value

0.9455

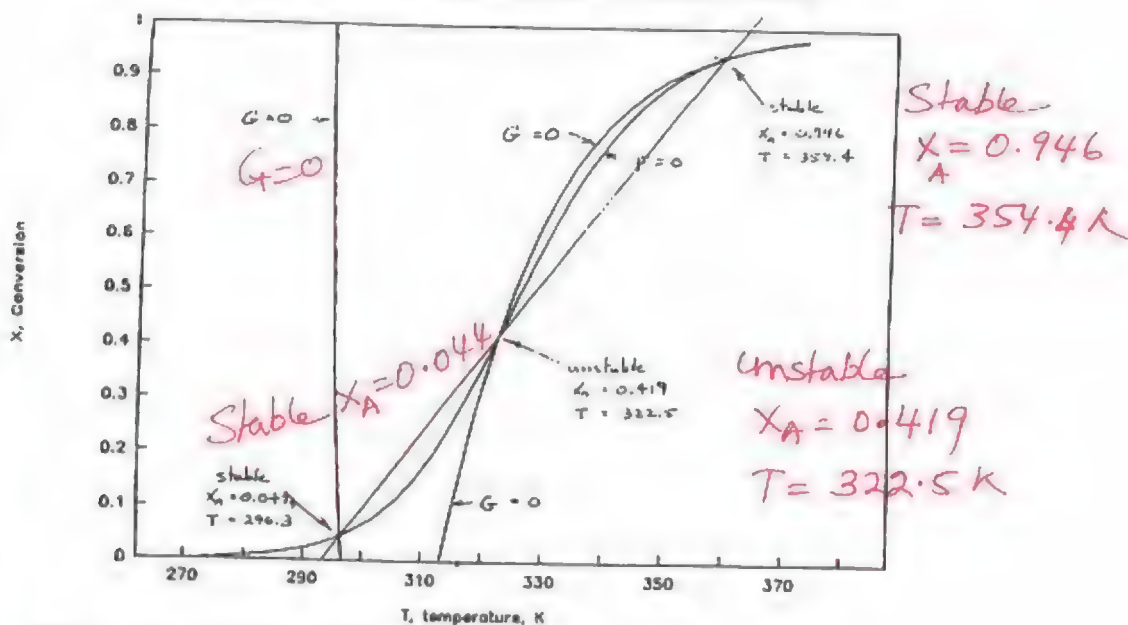
359.39

Roots are:

	X_A	T	
1	.00444	296.31	Stable
2	.4186	322.5	Unstable
3	.9455	359.39	Stable

This graph is also made from the equations showing the intersection of the two equations.

Conversion - Temperature Phase Plane



c) Separatrix-shown on Phase-Plane plot.

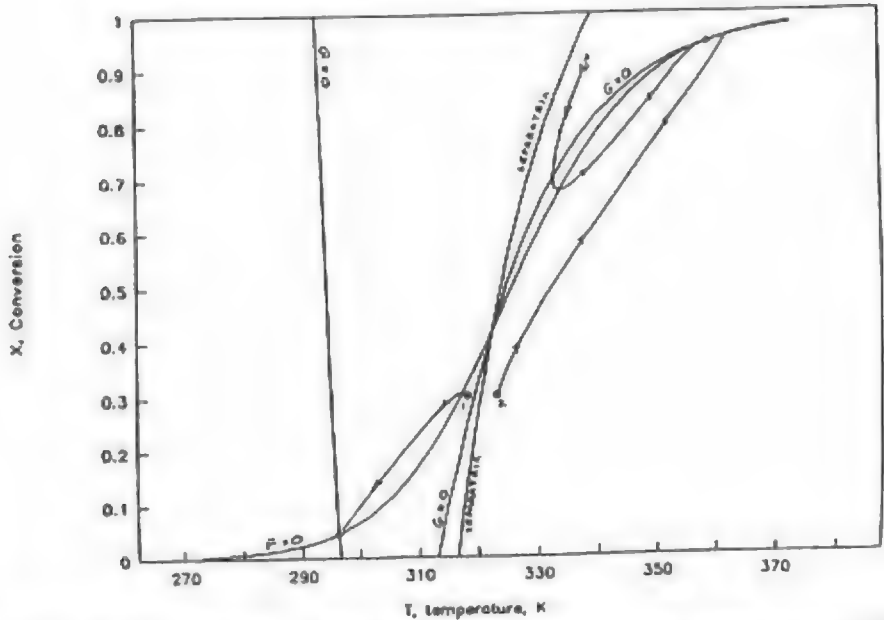
Found by solving:

$$\frac{dT}{dX} = \frac{G}{T} = \frac{(293.2 - T) + 0.1(70)k(1-X)}{-X + 0.1k(1-X)}$$

for various initial conditions at $X = 0$ or 1 , until trajectory went toward unstable point. Trials and errors were:

$X_i = 0, X_f = 0.414$		$X_i = 1, X_f = .424$	
T_i	T_f	T_i	T_f
317.2	327.2	337.2	318.1
316.2	318.2	337.4	318.3
316.7	324.5	339	320.6
316.6	324.2	340.4	315.4
316.5	322.4	339.5	322.5

Conversion - Temperature Phase Plane



Solution is unstable near (0.4186, 322.5), but integrations went smoothly except for one case.

POLYMATH will only integrate from lower to higher X, so equation was rewritten with $\gamma = 1 - X$, as

$$\frac{dT}{d\gamma} = -\frac{293.2 - T + 0.1(70)k\gamma}{-(1 - \gamma) + 0.1k\gamma}$$

d) Phase and time trajectories

The equations

$$\frac{dX}{d\theta} = -X + 0.1k(1 - X)$$

$$\frac{dT}{d\theta} = 293.2 - T + 0.1(70)k(1 - X)$$

were solved simultaneously with POLYMATH for the three cases.

Time responses are attached.

Discussion:

Case 1: (45°C, 0.3): Reaction "extinguishes" after a momentary increases in conversion.

Case 2:(50°C, 0.3): Reaction "ignites". T and X overshoot slightly. Final stabilization is rapid because of the high temperature (and hence k).

Case 3:(65°C, 0.9):Reactor "ignites" after significant dips in T and X. Reactant had to build up some before reaction could begin to raise temperature.

Time Trajectories

Case 3

Case 3 Adiabatic Reactor Dynamics

Integration Results

θ	X	T
0.0	0.9000	339.20
0.1250	0.8367	335.88
0.2500	0.7894	334.44
0.3750	0.7529	333.52
0.5000	0.7266	332.79
0.6250	0.7032	332.05
0.7500	0.6879	331.19
0.8750	0.6785	330.01
1.0000	0.6748	328.81
1.1250	0.6777	327.77
1.2500	0.6867	326.11
1.3750	0.7039	325.27
1.5000	0.7303	324.74
1.6250	0.7674	343.74
1.7500	0.8131	346.90
1.8750	0.8684	350.67
2.0000	0.8973	354.13
2.1250	0.9182	357.34
2.2500	0.9279	358.25
2.3750	0.9324	358.79
2.5000	0.9349	359.16

Separatrix

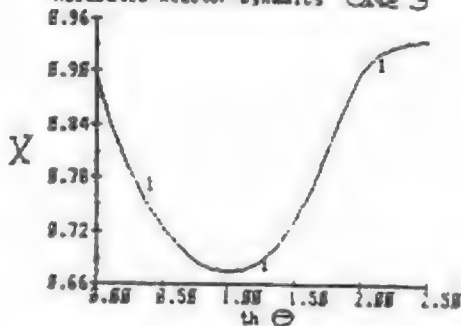
Upper

Integration Results

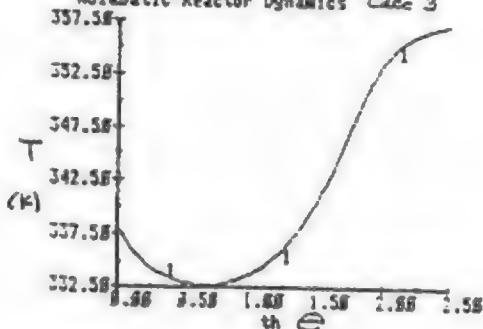
T	1-X
339.50	0.0
338.18	0.0280
336.93	0.0576
335.75	0.0864
334.63	0.1152
333.56	0.1440
332.55	0.1728
331.68	0.2016
330.69	0.2304
329.83	0.2592
329.02	0.2880
328.24	0.3168
327.49	0.3456
326.79	0.3744
326.11	0.4032
325.46	0.4320
324.83	0.4608
324.24	0.4896
323.66	0.5184
323.09	0.5472
322.58	0.5760

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Adiabatic Reactor Dynamics Case 3



Adiabatic Reactor Dynamics Case 3



Lower

Integration Results

X	T
0.0	316.50
0.0287	316.74
0.0414	316.99
0.0621	317.25
0.0828	317.50
0.1035	317.76
0.1242	318.02
0.1449	318.28
0.1656	318.50
0.1863	318.84
0.2070	319.13
0.2277	319.45
0.2484	319.75
0.2691	320.06
0.2898	320.37
0.3105	320.69
0.3312	321.02
0.3519	321.36
0.3726	321.70
0.3933	322.05
0.4140	322.40

Time Trajectories

Case 1

Case 1 Adiabatic Reactor Dynamics

Integration Results

Θ	X	T
0.0000	0.0000	318.28
0.3500	0.3249	317.52
0.7000	0.2907	316.14
1.0500	0.2554	314.97
1.4000	0.2152	312.75
1.7500	0.2415	310.78
2.1000	0.2158	308.79
2.4500	0.2158	306.80
2.8000	0.1985	305.13
3.1500	0.1668	303.57
3.5000	0.1457	302.42
3.8500	0.1272	301.89
4.2000	0.0985	300.15
4.5500	0.0877	298.22
4.9000	0.0799	296.78
5.2500	0.0713	295.44
5.6000	0.0661	297.64
5.9500	0.0616	297.52
6.3000	0.0588	297.26
6.6500	0.0551	297.06
7.0000	0.0528	296.98

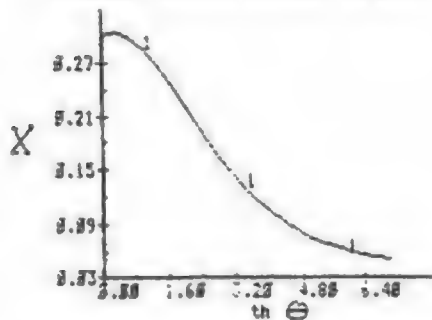
Case 2

Case 2 Adiabatic Reactor Dynamics

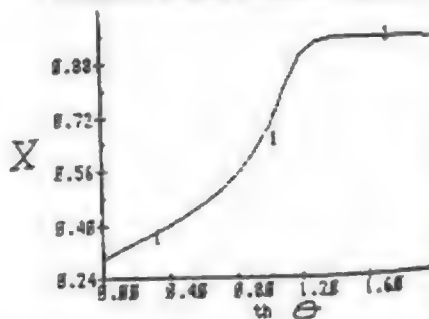
Integration Results

Θ	X	T
0.0000	0.0000	325.28
0.3500	0.3238	324.81
0.7000	0.3479	324.92
1.0500	0.3727	325.96
1.4000	0.3991	327.17
1.7500	0.4288	328.61
2.1000	0.4687	328.39
2.4500	0.4995	322.63
2.8000	0.5475	325.57
3.1500	0.6181	329.57
3.5000	0.6958	345.16
3.8500	0.8853	352.56
4.2000	0.9853	359.28
4.5500	0.9437	361.71
4.9000	0.9327	362.11
5.2500	0.9546	362.83
5.6000	0.9546	361.84
5.9500	0.9548	361.63
6.3000	0.9538	361.42
6.6500	0.9527	361.23
7.0000	0.9528	361.25

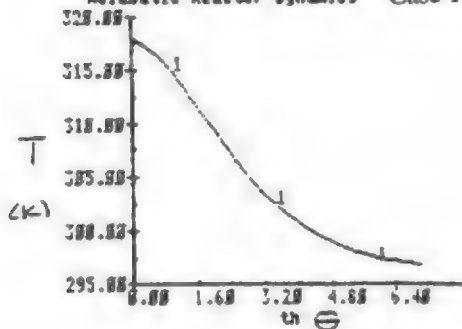
Adiabatic Reactor Dynamics CASE 1



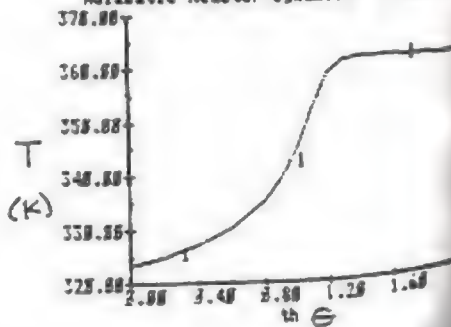
Adiabatic Reactor Dynamics CASE 2



Adiabatic Reactor Dynamics Case 1



Adiabatic Reactor Dynamics Case 2



R.L. Curl 10-30-66

a) Using only P as the solvent we come up with the following as the equations for the equilibrium conversion.

$$-r_A = k \left(C_A^2 - \frac{C_B^2}{K_e} \right)$$

$$-r_A = 0$$

$$C_A = \frac{C_B}{\sqrt{K_e}}$$

$$C_{A0}(1 - X_e) = \frac{C_{A0}X_e}{\sqrt{K_e}}$$

$$X_e = \frac{\sqrt{K_e}}{1 + \sqrt{K_e}}$$

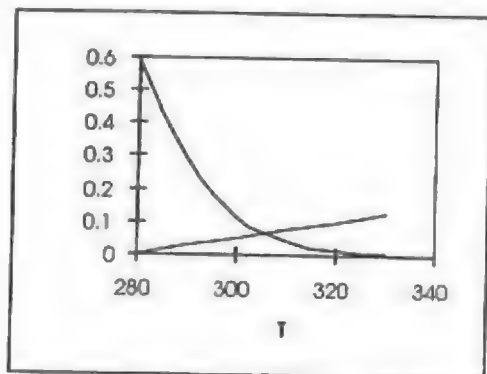
The equation for the energy balance part is this:

$$X_{eq} = \frac{C_{pA}(T - T_0) + 4 * C_{pB}(T - T_0)}{-\Delta H_{rx}}$$

We then need an equation for K_e . (Assuming that $K = 2$ when $T = 280K$)

$$K = 2 * \exp \left[\frac{\Delta H_{rx}}{R} \left(\frac{1}{280} - \frac{1}{T} \right) \right]$$

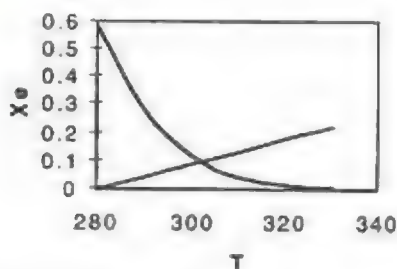
This graph is the result of these two equations:



We find the equilibrium temperature and conversion are 305.7K and 0.064.

CDP8-N **cont'd**

b) The same equations are used just the inert has been changed:



The equilibrium conversion and temperature are then 301.6K and 0.097

c) To find the place where the conversion is the maximum depending on the inert we must come up with the new energy equation where the inert amount can change.

$$X_{eb} = \frac{C_{PA}(T - T_0) + 4 * (y * C_{PP}(T - T_0) + (1 - y)C_{PQ}(T - T_0))}{-\Delta H_{rx}}$$

where y is the percentage of P in the inert. We find that the maximum occurs when only Q is fed in. $X = 0.097$

CDP8-Q

Gas phase reactions:



Write design equation in terms of flow rate since there are multiple reactions:

$$\frac{dF_A}{dV} = r_A$$

$$\frac{dF_B}{dV} = r_B$$

$$r_A = -k_1 C_A - k_2 C_A C_B^2$$

$$r_B = -k_2 C_A C_B^2 + k_1 C_A$$

$$k_1 = 2 * \exp\left[-\frac{E_1}{R}\left(\frac{1}{T} - \frac{1}{310}\right)\right]$$

$$k_2 = .2 * \exp\left[-\frac{E_2}{R}\left(\frac{1}{T} - \frac{1}{596}\right)\right]$$

$$C_A = C_i \frac{F_A T_0}{F_i T}$$

$$C_B = C_i \frac{F_B T_0}{F_i T}$$

Also write energy balance in terms other than conversion:

$$\frac{dT}{dV} = \frac{-\Delta H_{R1} * -r_{A1} - \Delta H_{R2} * -r_{A2}}{F_{A0} * C_{PA}}$$

The following is the POLYMATH program used:

8-119

CDP8-Q cont'd

8-o

Equations:

$$d(fa)/d(V) = ra$$

$$d(T)/d(V) = (-DHr1 - ra1 - DHr2 - ra2) / (fac * cpa)$$

$$d(fb)/d(V) = rb$$

$$DHr1 = -20000$$

$$DHr2 = -40000$$

$$fac = 100$$

$$cpa = 50$$

$$E1 = 5000$$

$$R = 1.987$$

$$E2 = 25000$$

$$cto = .5$$

$$ft = 100$$

$$To = 596$$

$$ct = cto$$

$$ca = cto * fa / ft * To / T$$

$$cb = ct * fb / ft * To / T$$

$$ra1 = -2 * \exp(-E1 / R * (1/T - 1/310)) * ca$$

$$ra2 = -.2 * \exp(-E2 / R * (1/T - 1/596)) * ca * cb^2$$

$$ra = ra1 + ra2$$

$$rb = -ra1 + ra2$$

$$V_0 = 0, \quad V_f = 7.12$$

Initial value

100

596

2

a)

POLYMATH gives the following table for the maximum temperature:

8-o

Variable

Variable	Initial value	Maximum value	Minimum value	Final value
V	0	7.12	0	7.12
fa	100	100	8.21231e-05	8.21231e-05
T	596	1129.84	596	1129.84
fb	0	94.3924	0	94.3924
DHr1	-20000	-20000	-20000	-20000
DHr2	-40000	-40000	-40000	-40000
fac	100	100	100	100
cpa	50	50	50	50
E1	5000	5000	5000	5000
R	1.987	1.987	1.987	1.987
E2	25000	25000	25000	25000
cto	0.5	0.5	0.5	0.5
ft	100	100	100	100
To	596	596	596	596
ct	0.5	0.5	0.5	0.5
ca	0.5	0.5	0.5	0.5
cb	0.5	0.5	2.16604e-07	2.16604e-07
ra1	0	0.265046	0	0.248965
ra2	-49.1661	-0.000156578	-49.1661	-0.000156578
ra	-0	-0	-2.96272	-5.76525e-05
rb	-49.1661	-0.000214231	-49.1661	-3.000214231
	49.1661	49.1661	9.89256e-05	9.89256e-05

8-120

CDP8-O

cont'd

$$V = 7.12 \text{ dm}^3$$

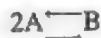
b) POLYMATH gives the following table for the maximum temperature:

$$V = 6.82 \text{ dm}^3$$

Variable	Initial value	Maximum value	Minimum value	Final value
V	0	6.82	0	6.82
fa	100	100	0.00145911	0.00145911
T	596	1005.52	596	1005.52
fb	0	95.2381	0	95.2381
DKr1	-20000	-20000	-20000	-20000
DKr2	-40000	-40000	-40000	-40000
fao	100	100	100	100
cpa	50	50	50	50
E1	5000	5000	5000	5000
R	1.987	1.987	1.987	1.987
E2	25000	25000	25000	25000
cto	0.5	0.5	0.5	0.5
ft	100	100	100	100
To	596	596	596	596
ct	0.5	0.5	0.5	0.5
ca	0.5	0.5	4.32431e-06	4.32431e-06
cb	0	0.282253	0	0.282253
ral	-49.1661	-0.0023735	-58.1183	-0.0023735
ra2	-0	-0	-1.4921	-0.000373347
ra	-49.1661	-0.00274685	-58.1526	-0.00274685
rb	49.1661	58.0922	0.00200016	0.00200016

CDP8-P

Gas phase



a)

$$\frac{dX}{dW} = \frac{-r_A}{F_{A0}}$$

$$-r_A = k \left[C_A^2 - \frac{C_B^2}{K_e} \right]$$

$$C_A = C_{A0}(1-X) \frac{T_0}{T}$$

$$C_B = C_{A0}X \frac{T_0}{T}$$

8-121

CDP8-P **cont'd**

$$K_e = \frac{X^2}{(1-X)^2}$$

$$k = 30 * \exp\left[\frac{E}{R}\left(\frac{1}{273} - \frac{1}{T}\right)\right]$$

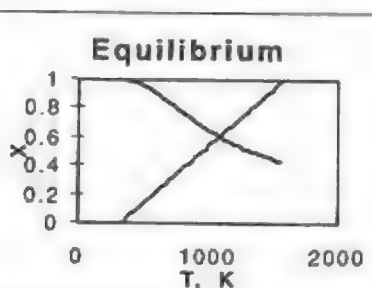
$$\frac{dX}{dW} = \frac{30 * \exp\left[\frac{4000}{1.987}\left(\frac{1}{273} - \frac{1}{T}\right)\right] \left[(.1)^2 (1-X)^2 - \frac{(.1)^2 X^2}{100 * \exp\left[\frac{-10000}{1.987}\left(\frac{1}{600} - \frac{1}{T}\right)\right]} \right]}{100}$$

$$K_e = \frac{X^2}{(1-X)^2}$$

$$X_{EB} = \frac{C_{pA}(T - T_0)}{-\Delta H_R} = 8 \times 10^{-4} (T - 323)$$

$$T = 323 + \frac{X(10000)}{8}$$

b)



At a temperature of 1081 K there is a equilibrium conversion of 0.61

c) $(0.98)(0.61) = 0.598$

The following POLYMATH program is used to determine how much catalyst weight is needed to achieve this conversion. We find that 42 kg of catalyst must be used.

CDP8-P cont'd

8-p

Equations:

$$d(w)/d(x) = fao / -ra$$

$$To = 323$$

$$fao = 100$$

$$Dhr1 = -10000$$

$$cpa = 8$$

$$E = 4000$$

$$R = 1.987$$

$$cao = .1$$

$$T = To + x * (-Dhr1) / cpa$$

$$ca = cao * (1 - x) * To / T$$

$$cb = cao * x * To / T$$

$$Ke = 100 * \exp(Dhr1 / R * (1/600 - 1/T))$$

$$k = 30 * \exp(E / R * (1/273 - 1/T))$$

$$ra = -k * (ca^2 - cb^2 / Ke)$$

$$x_0 = 0, \quad x_f = 0.598$$

Initial value

0

8-p

<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
x	0	0.598	0	0.598
w	0	42.1613	0	42.1613
To	323	323	323	323
fao	100	100	100	100
Dhr1	-10000	-10000	-10000	-10000
cpa	8	8	8	8
E	4000	4000	4000	4000
R	1.987	1.987	1.987	1.987
cao	0.1	0.1	0.1	0.1
T	323	1070.5	323	1070.5
ca	0.1	0.1	0.0121295	0.0121295
cb	0	0.0180433	0	0.0180433
Ke	133049	133049	2.50575	2.50575
k	93.9416	7292.68	93.9416	7292.68
ra	-0.939416	-0.12542	-2.93041	-0.12542

Chapter 9

- P9-1. An open-ended problem that requires students to create an original problem and solution.
- P9-2. "What if. . ." problem. These problems build in the **Living Example Problems** in this chapter. By this point in the point the student is in a position to carry out in-depth and meaningful parameter sensitivity studies. If there is only time to assign one or two parts of this problem I would choose part (a) and then either (d) or (e). However, one could rotate the assignments of (a) through (e) from year to year.
- P9-3. Although this problem on an explosion is a continuation of P8-3, it is not necessary to have worked P8-3 to work this problem. The students are asked to calculate the time before the reactor explodes.
- P9-4. Alternative problem to P9-3.
- P9-5. Straight forward problem on heat effects in a semibatch reactor.
- P9-6. Another one that involves a lot of thinking and not a large number of calculations.
- P9-7. A straight forward problem concerning an adiabatically operated batch reactor. Alternate to P9-8 and P9-9.
- P9-8. Straight forward adiabatic batch reactor calculation.
- P9-9. Similar to P8-19, but with different specific reaction rates.
- P9-10. Start up of a CSTR.
- P9-11. Fairly, straight forward semibatch reactor problem. The volumetric feed rate must be varied, but within certain limits.
- Problems P9-12, P9-13, and P9-14. involve the use of controllers during the operation of a CSTR. These problems provide excellent *What if. . .* problems because the student can vary the control parameters and observe the various outcomes.
- P9-15. <Prof. Fogler: Anything going here?>
- P9-16. The point of this problem is that what we learned in chapter 8 about the different multiple steady states being stable is not necessarily true. One will find in this problem that the extinction temperature is not exceeded, yet we still fall from the upper steady states to the lower steady states. This problem also allows the student to explore the parameter space.

P9-17. Living Example Problem 8-12. Can serve as a basis to study the adiabatic operation of a batch reactor.

P9-18. Straight forward problem on parallel reactions in a semibatch reactor.

Summary

	Assigned	Alternates	Difficulty	Time	Solution Given	Do
P9-1	AA					
• P9-2	AA	(a),3,4,7	MD	75	Yes	
P9-3	AA	2(a),4	SF	60	Yes	
P9-4	AA	2(a),3	FSF	60	Yes	
• P9-5	AA	11,18,A	FSF	75	Yes	
P9-6	O		FSF	45	Yes	
• P9-7	AA	2(a),8,17	SF	60	Yes	
P9-8	AA	2(a),7,17	SF	60	Yes	
P9-9	I		MD	60		
P9-10	G	10b/a	FSF	40/40	Yes	
P9-11	AA	5,18,A	FSF	60	Yes	
• P9-12	G/AA	13,14,15,B	SF	45	Yes	
P9-13	G/AA	12,14,15,B	SF	30	Yes	
P9-14	G/AA	12,13,15,B	SF	30	Yes	
P9-15	G/AA	12,13,14,B	MD	90	Yes	
• P9-16	G		MD	75	Yes	
P9-17	AA	(a),7,8	FSF	60	Yes	
P9-18	AA	5,11,A	FSF	90	Yes	
CDP9-A	AA	5,11,18	FSF	75	Yes	
CDP9-B	AA	12,13,14,15	FSF	75	Yes	
CDP9-C						
CDP9-D						
CDP9-E						
CDP9-F						
CDP9-G						
CDP9-H						
CDP9-I						

Assigned

- = Always assigned, AA = Always assign one from the group of alternates,
- O = Often, I = Infrequently, S = Seldom, G = Graduate level

Alternates

In problems that have a dot in conjunction with AA means that one of the problems, either the problem with a dot or any one of the alternates are always assigned.

Time

Approximate time in minutes it would take a B/B* student to solve the problem.

Difficulty

SF = Straight forward reinforcement of principles (plug and chug)

FSF = Fairly straight forward (requires some manipulation of equations or an intermediate calculation).

IC = Intermediate calculation required

M = More difficult

OE = Some parts open-ended.

Note the letter problems are found on the CD-ROM. For example A = CDP1-A.

Summary Table Ch-9

	Safety	Batch	Semi-Batch	Unsteady Start-up	Control
Review of Definitions and Assumptions					
Open-ended	2(a)	17(b,c)	18(b,c)	2(b,c),16(f)	2(d,e)
Straight forward	3	7,8			12,13,14
Fairly Straight Forward	4	17	5,6,11,18,A	2(b),2(c),10	B
More Difficult	2(a)			9,16	15
Critical Thinking					

P9-1 No solution will be given

P9-2

a) To show that no explosion occurred without cooling failure.
Isothermal operation throughout ($T = 175^\circ\text{C}$)

Maximum cooling rate:

$$Q_r = UA[448 - 298] = 142 * 150 \\ = 21300 \text{ BTU/min}$$

Maximum Q_g at $t = 0$ (maximum concentration and reaction rate)

$$Q_g = k \frac{N_{A0} N_{B0}}{V^2} * V(-\Delta H_{Rx}) \\ = 0.0001167 \left[\frac{9.04 * 33}{5.119} \right] 2.34 * 10^6 \\ = 15914.2 \text{ BTU/min}$$

For all t :

$$Q_g < Q_r \quad \text{No explosion}$$

To show that no explosion occurs with cooling shut down for 10 min. after 12 hrs.
Isothermal operation for 12 hrs. (at $T = 175^\circ\text{C}$)

$$t = \left[\frac{V}{kN_{A0}} \right] \left(\frac{1}{\theta_B - 2} \right) \ln \frac{\theta_B - 2x}{\theta_B(1-x)} \\ \frac{\theta_B - 2x}{\theta_B(1-x)} = 1.276 \\ 3.64 - 2x = 1.276 * 3.64(1-x) \\ x = 0.38$$

Q_g at $t = 12$ hrs.

$$Q_g = k \frac{N_{A0}(1-x)N_{B0}(\theta_B - 2x)}{V} (-\Delta H_{Rx}) \\ = 0.0001167 \left[\frac{9.04^2(1-.38)(\theta_B - 2 * .38)}{5.119} \right] 2.34 * 10^6 \\ = 77844 \text{ BTU/min.}$$

Adiabatic operation for 10 min. $UA = 0$

After 10 minutes

P9-2 cont'd

$$x = 0.385, T = 184^{\circ}\text{C}$$

$$Q_c = 10000 \text{ BTU/min.}$$

When we restart the cooling flow rate

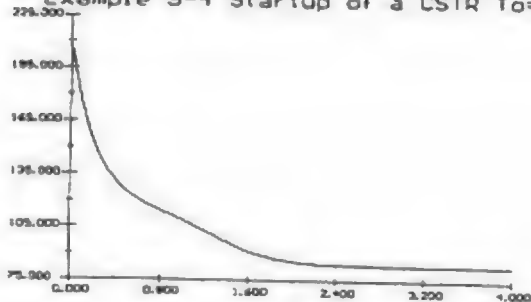
$$Q_{c,\text{max}} = 21,300 \text{ BTU/min.}$$

Temperature will drop to 175°C

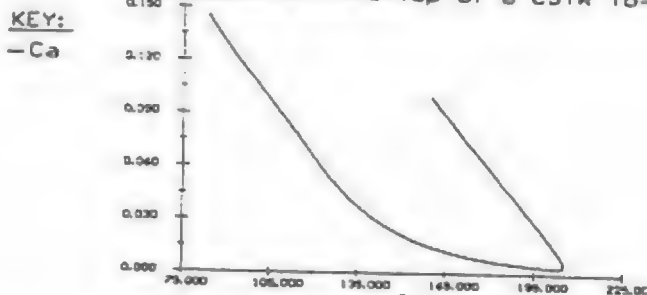
No explosion

b) Using the same code as seen in Example 9-4, we were able to change the various parameters. The two graphs we have show $T_0 = 70$ and 120°C , $T_1 = 160$ and 40°C , and $C_{a1} = .1$ and $.2$. Each set of parameters had a Temperature time trajectory and a temperature-concentration phase plane. These are the four graphs.

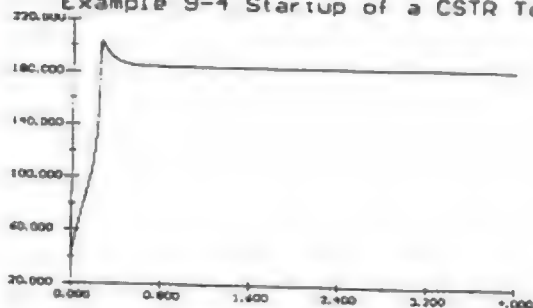
Example 9-4 Startup of a CSTR $T_0=70$, $T_1=160$, $C_{a1}=.1$



Example 9-4 Startup of a CSTR $T_0=70$, $T_1=160$, $C_{a1}=.1$



Example 9-4 Startup of a CSTR $T_0=120$, $T_1=40$, $C_{a1}=.2$

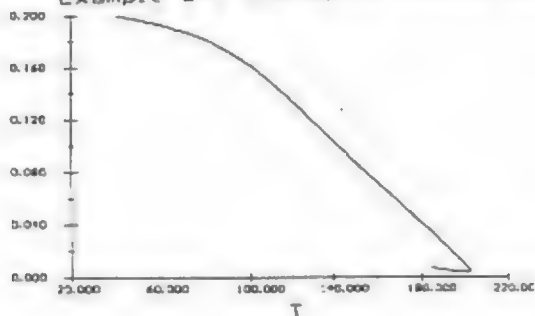


P9-2 cont'd

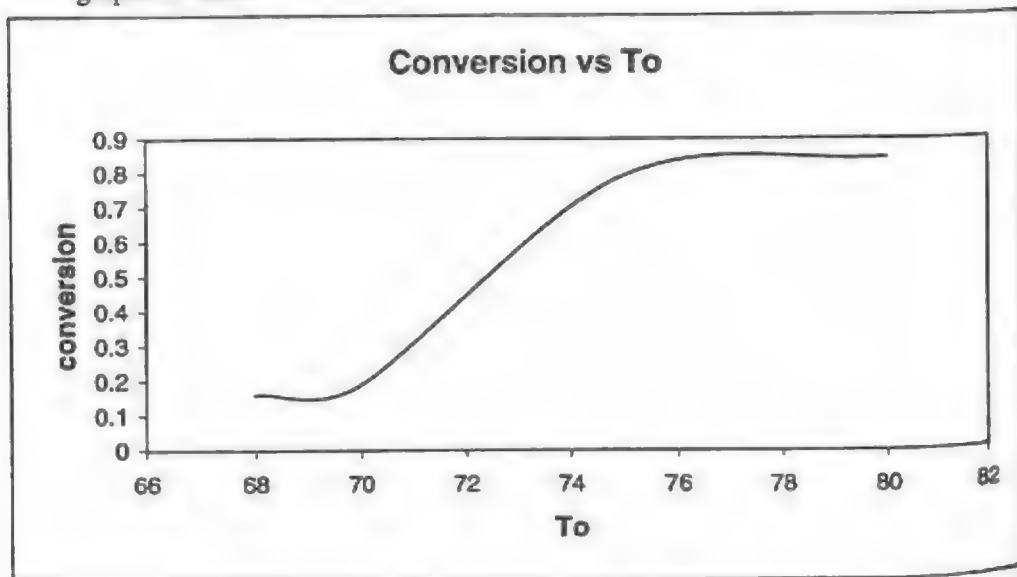
Example 9-4 Startup of a CSTR $T_0=120$ $T_1=40$ $Ca=0.2$

KEY:

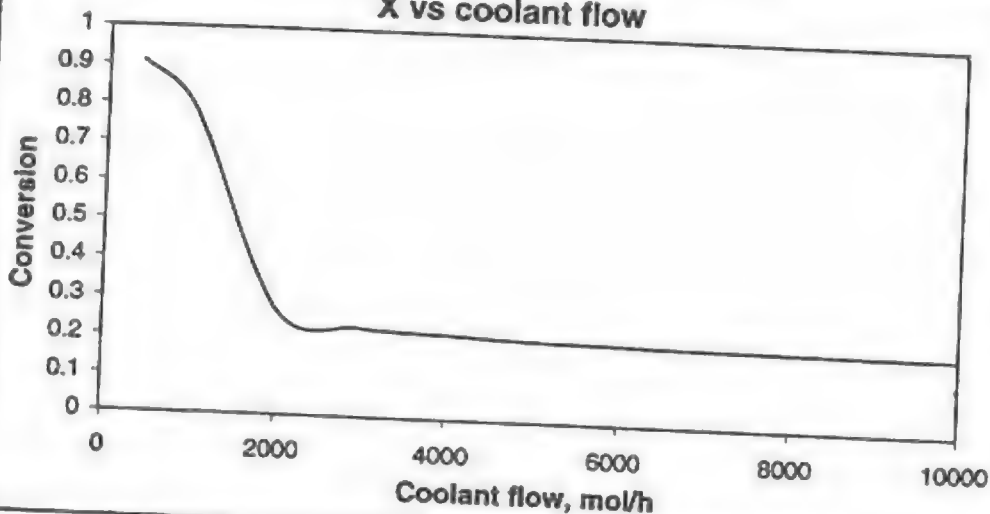
-Ca



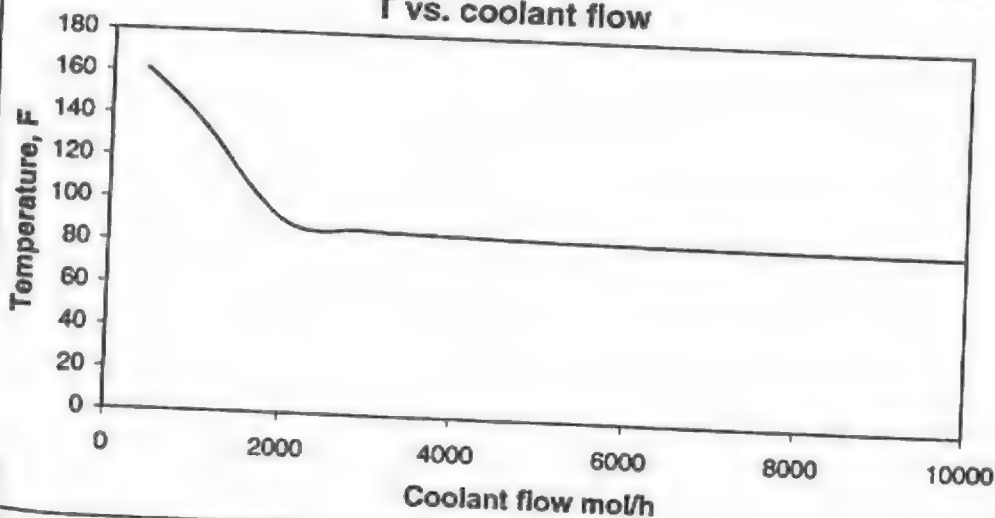
c) Using the code from Example 9-5, we could produce the following graphs either by changing T_0 and finding the steady-state conversion or changing the coolant flow rate and finding the steady-state conversion and temperature. These are the graphs of those.



X vs coolant flow



T vs. coolant flow

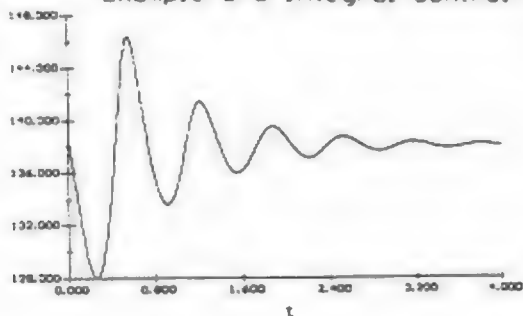


d) Using the code from Example 9-6, we can determine the value of k_c for which the reactor will fall to the lower steady-state and when it becomes unstable. The following two graphs show those points when $k_c = .2$ and 24 respectively. The third graph shows what happens when $T_0 = 65$. It becomes unstable at a much lower temperature.

P9-2 cont'd

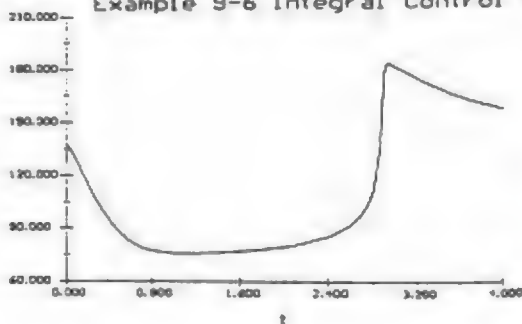
Example 9-6 Integral Control $k_c=24$

KEY:
-T



Example 9-6 Integral Control $T_0=65, k_c=24$

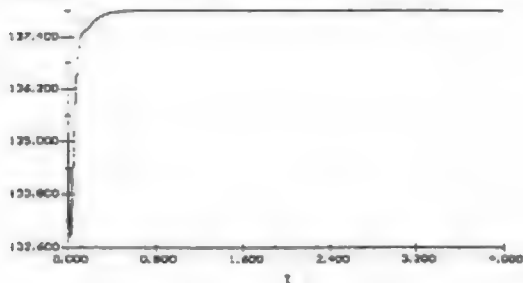
KEY:
-T



e) Using the code from Example 9-7, we can change the values of k_c and τ_i and find values that produce the lowest oscillations and the quickest return to steady-state and getting $k_c = 150$ and $\tau_i = .1$. The following graph shows the result.

Example 9-7 PI Controller $k_c=150$ $\tau_i=.1$

KEY:
-T



P9-3

Find time to explosion

For the unsteady-state, we assume the following:

- (i) The inlet is closed, but the outlet is not closed
- (ii) Operation is adiabatic, and PV terms are negligible so that $H = U$

Equation 8-61 reduces to:

$$(-\Delta H_R)(-r_A V) = N_A C_{pA} \frac{dT}{dt}$$

$$(-\Delta H_R)(k N_A) = N_A C_{pA} \frac{dT}{dt}$$

$$\frac{dT}{dt} = \frac{\Delta H_{R298}}{C_{pA}} k(T)$$

$$k = .53 \exp \left(44499 \left(\frac{1}{970} - \frac{1}{T} \right) \right) / 60 \text{ min.}$$

POLYMATH

The equations:

$$d(t1)/dt = -dh/k/cpa$$

$$dh = -336$$

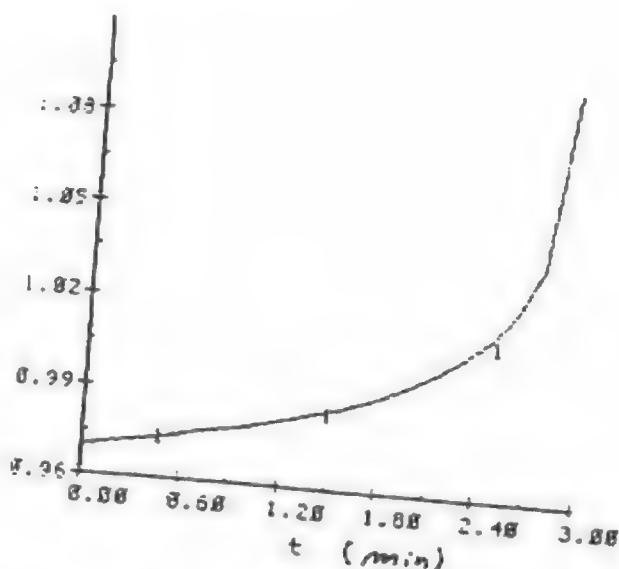
$$cpa = .38$$

$$k = .53 \cdot \exp(44499 \cdot (1/978 - 1/t1)) \cdot .68$$

$$\text{Initial values: } t_1 = 0.8, \quad t_{1g} = 978.88$$

$$\text{Final value: } T_g = 2.9888$$

$\frac{t - t_1}{t_1}$
 $\cdot 10^{-3}$
 $T (^{\circ}R)$



P9-4

Mole balance:

$$F_{A0} - F_A + Vr_A = \frac{dN_A}{dt}$$

$$F_{B0} - F_B + Vr_B = \frac{dN_B}{dt}$$

$$F_{C0} - F_C + Vr_C = \frac{dN_C}{dt}$$

There is no A leaving the reactor so $F_A = 0$. There is no B or C entering the reactor so F_{B0} and $F_{C0} = 0$. The amount of B and C leaving is equal to the reaction rate so $F_B = Vr_B$ and $F_C = Vr_C$. Simplifying:

$$F_{A0} + Vr_A = \frac{dN_A}{dt}$$

$$\frac{dN_B}{dt} = 0$$

$$\frac{dN_C}{dt} = 0$$

Rate law:

$$r_A = -kC_A$$

Stoichiometry:

$$C_A = \frac{N_A}{V}$$

Simplifying:

$$r_A V = kN_A$$

Energy balance:

$$\frac{dT}{dt} = \frac{r_A V \Delta H_{rx} - F_{A0} C_{pA} (T_0 - T)}{N_A C_{pA}}$$

Evaluate the parameters:

P9-4 cont'd

$$\ln\left(\frac{.19}{.32}\right) = \frac{E}{R}\left(\frac{1}{800} - \frac{1}{400}\right)$$

$$E = 3467$$

$$k = .19 \exp\left[\frac{3467}{8.314}\left(\frac{1}{400} - \frac{1}{T}\right)\right]$$

$$\Delta H(400) = -8 \text{ kJ/mol} = \Delta H(800) = \Delta H(1200) = \Delta H(T)$$

Assume a heat capacity for A of 20 J/molK and assume there is no A already in the reactor. We can plug these equations into POLYMATH and get this answer.

9-4

Equations:

$$d(na)/dt = fao - vra$$

$$d(T)/dt = (vra \cdot Dhrl) - fao \cdot cpa \cdot (T - To) / (na \cdot cpa)$$

$$fao = 100$$

$$Dhrl = -8000$$

$$cpa = 20$$

$$To = 400$$

$$k = .19 \cdot \exp(3467/8.314 \cdot (1/400 - 1/T))$$

$$vra = -k \cdot na$$

$$t_0 = 0, \quad t_f = 100$$

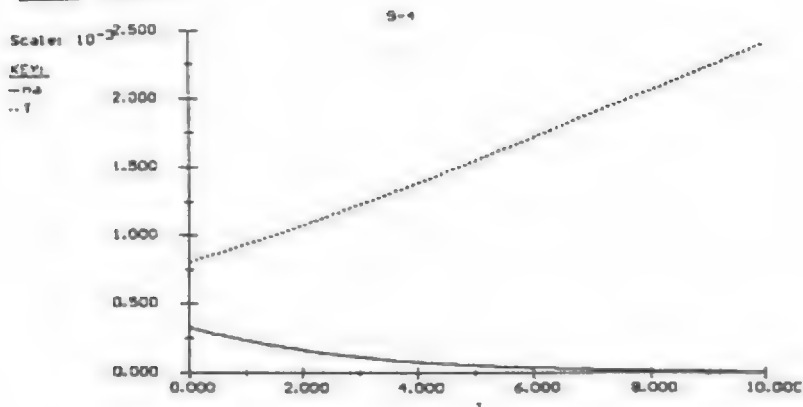
9-4

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	100	0	100
na	1e-09	326.125	1e-09	312.512
T	400	801.383	400	800
fao	100	100	100	100
Dhrl	-8000	-8000	-8000	-8000
cpa	20	20	20	20
To	400	400	400	400
k	0.19	0.320276	0.19	0.319988
vra	-1.9e-10	-1.9e-10	-101.769	-130

$$N_A = 326.125$$

When the flow is turned off, $F_{A0} = 0$ and we get this graph of T and N_A .

P9-4 cont'd



P9-5

Semibatch problem

Part (a)

Mole balance :

$$\frac{dN_a}{dt} = r_a V$$

$$\frac{dN_b}{dt} = r_a V + F b_0$$

$$\frac{dN_c}{dt} = -r_a V$$

Rate law :

$$-r_a = k(T) \cdot C_a \cdot C_b$$

Stoichiometry :

$$C_a = \frac{N_a}{V}$$

$$C_b = \frac{N_b}{V}$$

$$C_c = \frac{N_c}{V}$$

IF ($t < 50$) THEN ($V = V_0 + v \cdot t$) ELSE ($V = V_0 + 50$) where $V_0 = 50 \text{ dm}^3$, $v = 1 \text{ dm}^3/\text{min}$

Combining :

$$-r_a = k(T) \cdot \frac{N_a}{V} \cdot \frac{N_b}{V}$$

P9-5 cont'd

$$k(T) = k_o \cdot \exp \left[\frac{E}{R} \left(\frac{1}{T_o} - \frac{1}{T} \right) \right]$$

where $E = 10000 \text{ cal/mol}$,

$$k_o = 0.01 \text{ dm}^3/\text{mol} \cdot \text{min}, \\ T_o = 300 \text{ K}$$

$$R = 1.987 \text{ cal/mol} \cdot \text{K}$$

Energy balance :

$$\frac{dT}{dt} = \frac{Q - W_s - \sum F_{io} \cdot C_{pi} \cdot (T - T_{io}) + (-\Delta H_{rx}(T)) \cdot (-r_a \cdot V)}{\sum N_i \cdot C_{pi}}$$

$$\text{where } Q = W_s = 0$$

$$\Delta H_{rx}(T) = \Delta H_{rx}(T_{ref}) + \Delta C_p(T - T_{ref})$$

$$\Delta C_p = \frac{c}{a} \cdot C_p - \frac{b}{a} \cdot C_{pb} - C_{pa} = 30 - 15 - 15 = 0$$

$$\Delta H_{rx}(273) = [(-41) - (-20) - (-15)] \cdot 10^3 = -6000 \text{ cal/mol}$$

$$\Delta H_{rx}(T) = -6000 \text{ cal/mol}$$

$$\sum F_{io} \cdot C_{pi} \cdot (T - T_{io}) = F_{bo} \cdot (15) \cdot (T - 323)$$

$$\begin{aligned} \sum N_i \cdot C_{pi} &= N_a C_{pa} + N_b C_{pb} + N_c C_{pc} \\ &= 15N_a + 15N_b + 30N_c \end{aligned}$$

POLYMATH solution P9-5B part(a)

P9-5 cont'd

P9-5 (a)

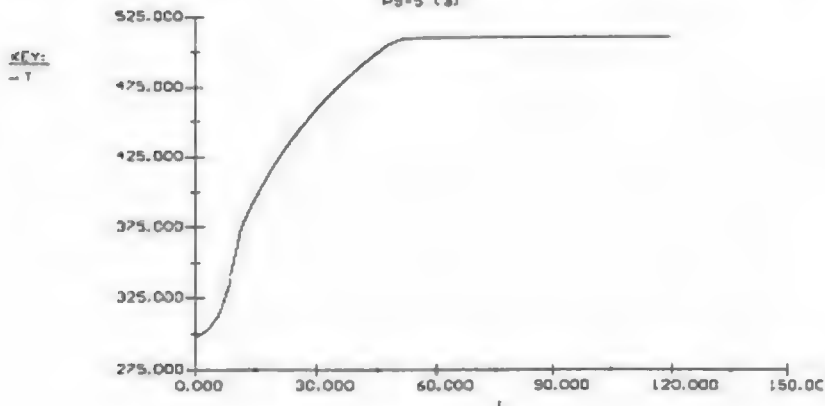
Equations:

	<u>Initial value</u>
$d(Na)/d(t) = ra \cdot V$	500
$d(Nb)/d(t) = (ra \cdot V) + Fbo$	0
$d(Nc)/d(t) = -ra \cdot V$	0
$d(T)/d(t) = ((6000 \cdot (-ra \cdot V)) - (Fbo \cdot 15 \cdot (T - 323))) / ((15 \cdot Na) + (15 \cdot Nb) + (30 \cdot Nc))$	298
$d(x)/d(t) = (-ra \cdot V) / Nao$	0
$Fbo = \text{if}(t < 50) \text{ then } (10) \text{ else } (0)$	
$Nao = 500$	
$Cbo = 10$	
$k = 0.01 \cdot \exp((10000/1.987) \cdot ((1/300) - (1/T)))$	
$vo = Fbo / Cbo$	
$V = \text{if}(t < 50) \text{ then } (50 + (vo \cdot t)) \text{ else } (100)$	
$ra = -k \cdot Na \cdot Nb / (V \cdot V)$	
$t_0 = 0, \quad t_f = 120$	

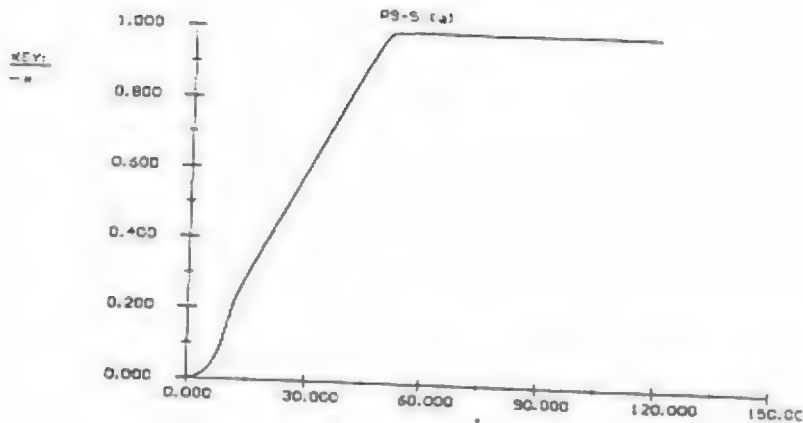
P9-5 (a)

<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
t	0	120	0	120
Na	500	500	0.139723	0.139723
Nb	0	42.6509	0	0.139723
Nc	0	499.86	0	499.86
T	298	510.444	298	510.444
x	0	0.999721	0	0.999721
Fbo	10	10	0	0
Nao	500	500	500	500
Cbo	10	10	10	10
k	0.00893518	10.0851	0.00893518	10.0851
vo	1	1	0	0
V	50	100	50	100
ra	-0	-0	-0.352221	-1.96886e-05

P9-5 (a)



P9-5 cont'd



Part (b)

As for part(a) except

Energy balance :

$$\frac{dT}{dt} = \frac{Q - W_s - \sum F_{i0} C_{pi} (T - T_{i0}) + (-\Delta H_{rx}(T)) (-r_a V)}{\sum N_i C_{pi}}$$

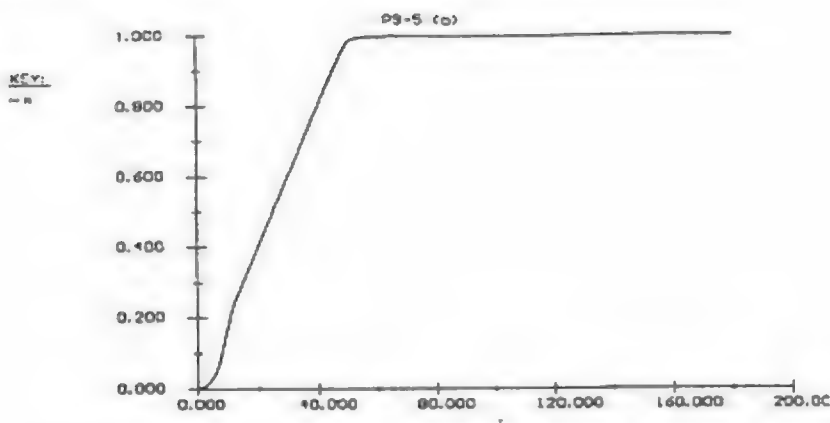
where $Q = UA(T_a - T)$

$UA = 100, T_a = 323$

P9-5 (b)

Variable	Initial value	Maximum value	Minimum value	Final value
τ	0	180	0	180
N_a	500	500	0.397438	0.397438
N_b	0	40.9551	0	0.397438
N_c	0	499.603	0	499.603
T	298	476.955	298	389.364
x	0	0.999205	0	0.999205
F_{b0}	10	10	0	0
UA	100	100	100	100
T_a	323	323	323	323
N_{a0}	500	500	500	500
C_{b0}	10	10	10	10
k	0.00893518	5.04699	0.00893518	0.470049
v_0	1	1	0	0
V	50	100	50	100
z_a	-0	-0	-0.341013	-7.42476e-06

P9-5 cont'd



Part (c)

As for part (b) except :

Rate law : $-ra = k1(T).Ca.Cb - k2(T).Cc$

Combining : $-ra = k1(T). \left(\frac{Na}{V} . \frac{Nb}{V} \right) - k2(T). \left(\frac{Nc}{V} \right)$

$$k2(T) = ko.exp \left[\frac{E}{R} \left(\frac{1}{To} - \frac{1}{T} \right) \right] \text{ where } E = 16000, R = 1.987,$$

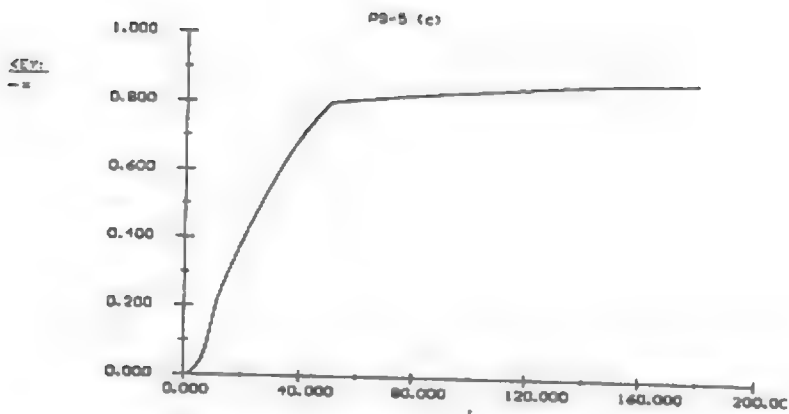
$$ko = 10, To = 300$$

P9-5 (c)

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	180	0	180
Na	500	500	62.9262	62.9262
Nb	0	102.378	0	62.9262
Nc	0	437.074	0	437.074
T	298	444.058	298	383.479
x	0	0.874148	0	0.874148
Fbo	10	10	0	0
UA	100	100	100	100
Ta	323	323	323	323
Nao	500	500	500	500
Cbo	10	10	10	10
k1	0.00893518	2.30959	0.00893518	0.385471
k2	8.35152e-05	0.604861	8.35152e-05	0.0344816
vo	1	1	0	0
v	50	100	50	100
ra	-0	-0	-0.336444	-0.00192523

9-16

P2-5 cont'd



P2-6B

Part (a)

Mol balance : $\frac{dN_A}{dt} = r_A V$

Rate law : $-r_A = k C_A$

But $C_A V = N_A$

$$\frac{dN_A}{dt} = -k N_A$$

$$\int_{N_{Ao}}^{N_A} \frac{dN_A}{N_A} = -k \int_0^t dt$$

$$\ln \frac{N_A}{N_{Ao}} = -k \cdot t$$

$$N_A = N_{Ao} e^{-kt}$$

where $N_{Ao} = 0.5 \times 50 = 25$

Energy balance :

$$\frac{dT}{dt} = \frac{Q - W_s - \sum F_{i0} C_{pi} (T - T_{i0}) + (-\Delta H_{rx})(-r_A V)}{\sum N_i C_{pi}} = 0 \quad \text{constant } T$$

$$Q = W_s = 0$$

$$\sum F_{i0} C_{pi} (T - T_{i0}) = (-\Delta H_{rx})(-r_A V)$$

$$F_{C0} C_{pc} (T - T_{i0}) = (-\Delta H_{rx})(k N_A)$$

$$= (-\Delta H_{rx})(k N_{Ao} e^{-kt})$$

9-17

P9-6 cont'd

$$\begin{aligned} F_{co} &= \frac{(-\Delta H_{rx})(kN_{ao}.e^{-b})}{C_{pc}.(T - T_{io})} \\ &= \frac{25000 \times 0.00012 \times 25 \times \exp(-0.00012 \times 2 \times 3600)}{0.5.(100 - 80)} \\ &= 3.16 \text{ lb/s} \end{aligned}$$

Part (b)

$$\lambda_v = 1000 \text{ Btu / lb}$$

$$N_{ao} = 25 \text{ lb/mol}$$

$$V_o = 300 \text{ ft}^3 \text{ of which } 250 \text{ ft}^3 \text{ is solvent}$$

$$\frac{dT}{dt} = 0$$

$$F_s. \lambda_v = (-\Delta H_{rx})(-r_a.V)$$

$$\begin{aligned} F_s &= \frac{(-\Delta H_{rx}).(kN_{ao}.e^{-b})}{\lambda_v} = \frac{25000 \times 0.00012 \times 25 \times \exp(-0.00012 \times 2 \times 3600)}{1000} \\ &= 0.0316 \text{ lb/s} \end{aligned}$$

P9-7_a

Batch problem

$$\text{Mol balance :} \quad N_{ao} \frac{dX}{dt} = -r_a V \quad C_{ao} \frac{dX}{dt} = -r_a$$

$$\text{Rate law :} \quad -r_a = k_1.C_a^{1/2}C_b^{1/2} - k_2.C_c$$

$$\text{Stoichiometry :} \quad C_a = C_{ao}(1-X) = 0.1(1-X)$$

$$C_b = C_{ao}(1.25-X) = 0.1(1.25-X)$$

$$C_c = C_{ao}(0+X) = 0.1X$$

9-18

P2-7 cont'd

$$k_1(T) = k_o \cdot \exp\left[\frac{E}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right] \quad \text{where} \quad E = 100000 \text{ J/mol.}, R = 8.314 \text{ J/mol.K.},$$

$$k_o = 0.002 \text{ /s}, T_o = 373 \text{ K}$$

$$k_2(T) = k_o \cdot \exp\left[\frac{E}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right] \quad \text{where} \quad E = 150000 \text{ J/mol.}, R = 8.314 \text{ J/mol.K.},$$

$$k_o = 0.00003 \text{ /s}, T_o = 373 \text{ K}$$

Energy balance :

$$\frac{dT}{dt} = \frac{(-\Delta H_{rx}(T)) \cdot (-r_a \cdot V)}{\sum N_i \cdot C_{pi}}$$

$$\text{where } \sum N_i \cdot C_{pi} = N_{ao}(\sum \theta_i C_{pi} + \Delta C_p X)$$

$$\Delta C_p = \frac{c}{a} \cdot C_{pc} - \frac{b}{a} \cdot C_{pb} - C_{pa} = 40 - 25 - 25 = -10$$

$$\sum \theta_i \cdot C_{pi} = \frac{C_{ao}}{C_{ao}} \cdot C_{pa} + \frac{C_{bo}}{C_{ao}} \cdot C_{pb} + \frac{C_{co}}{C_{ao}} \cdot C_{pc}$$

$$= 25 + 0.125/0.1 \cdot 25 + 0 = 56.25$$

$$\Delta H_{rx}(T) = \Delta H_{rx}(T_{ref}) + \Delta C_p(T - T_{ref})$$

$$= -40000 - 10 \cdot (T - 298)$$

$$V = \frac{N_{ao}}{C_{ao}}$$

subs

$$\frac{dT}{dt} = \frac{[40000 + 10 \cdot (T - 298)] \cdot \left(-r_a \cdot \frac{N_{ao}}{C_{ao}}\right)}{N_{ao}(56.25 - 10X)}$$

cancelling

$$\frac{dT}{dt} = \frac{[40000 + 10 \cdot (T - 298)] \cdot \left(\frac{-r_a}{0.1}\right)}{(56.25 - 10X)}$$

⇒ POLYMATH

9-19

P9-7 cont'd

Equations:

$$d(x)/d(\tau) = (-r_a)/0.1$$

Initial value

0

$$d(T)/d(\tau) = (40000 + (10 \cdot (T - 298))) \cdot (-r_a) \cdot (1/0.1) / (56.25 - (10 \cdot x))$$

373

$$k_1 = 0.002 \cdot \exp((100000/8.314) \cdot ((1/373) - (1/T)))$$

$$C_a = 0.1 \cdot (1 - x)$$

$$C_b = 0.1 \cdot (1.25 - x)$$

$$k_2 = 0.00003 \cdot \exp((150000/8.314) \cdot ((1/373) - (1/T)))$$

$$C_c = 0.1 \cdot x$$

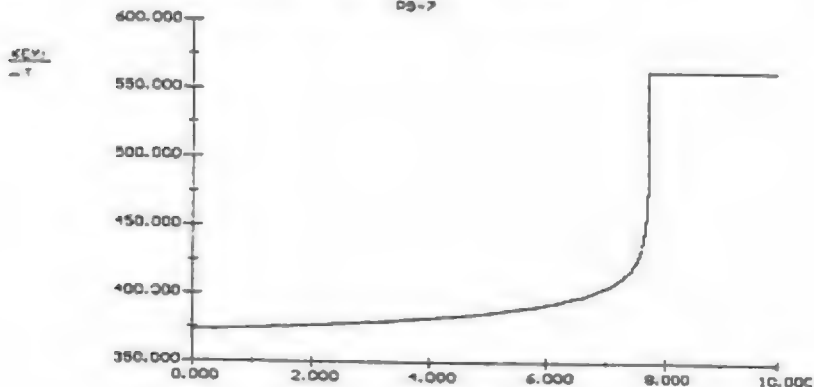
$$r_a = -(k_1 \cdot (C_a \cdot 0.5) \cdot (C_b \cdot 0.5)) - (k_2 \cdot C_c)$$

$$\tau_0 = 0, \quad \tau_f = 10$$

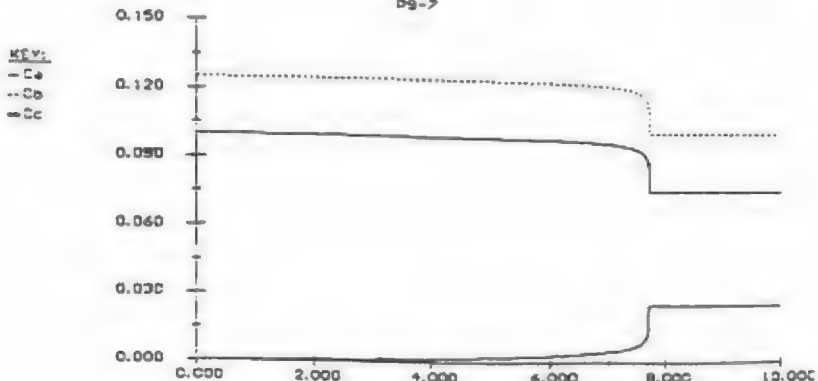
P9-7

Variable	Initial value	Maximum value	Minimum value	Final value
τ	0	10	0	10
x	0	0.250483	0	0.250483
T	373	562.918	373	562.918
k_1	0.002	106.136	0.002	106.136
C_a	0.1	0.1	0.0749517	0.0749517
C_b	0.125	0.125	0.0999517	0.0999517
k_2	3e-05	366.751	3e-05	366.751
C_c	0	0.0250483	0	0.0250483
r_a	-0.000223607	3.90133e-09	-1.76905	3.89138e-09

P9-7



P9-7



P9-7 cont'd

Check answer: $\frac{C_c}{\sqrt{C_a}\sqrt{C_b}} = \frac{k_1}{k_2}$

$$\frac{0.02504}{\sqrt{0.07495} \times \sqrt{0.09995}} = \frac{1.06}{3.67} = 0.289$$

P9-8_R

Adiabatic, batch, reversible.

Design equation: $N_{A0} \frac{dX}{dt} = -r_A V$

Rate law: $-r_A = k_1 \left[C_A - \frac{C_S^2}{K_e} \right]$

Stoichiometry: $C_A = C_{A0} (1 - X), \quad C_B = -2 \cdot C_{A0} \cdot X$

Combining: $C_{A0} \frac{dX}{dt} = k_1 \left[C_{A0}(1 - X) - \frac{4C_{A0}^2(1 - X)^2}{K_e} \right]$

$$\frac{dX}{dt} = k_1 \left[(1 - X) - \frac{4C_{A0}(1 - X)^2}{K_e} \right]$$

Parameter evaluation: $E = \frac{\ln \frac{k_1}{k_2}}{\frac{1}{R \cdot T_2} - \frac{1}{R \cdot T_1}} = \frac{\ln \frac{0.217}{0.324}}{\frac{1}{8.314(340)} - \frac{1}{8.314(300)}} = 8498 \text{ J/mol}$

$$k_1 = 0.217 \exp \left[\frac{8498}{8.314} \left(\frac{1}{340} - \frac{1}{T} \right) \right]$$

$$\ln \frac{K_e(T)}{K_e(300)} = \frac{\Delta H_{rx}}{R} \left(\frac{1}{300} - \frac{1}{T} \right)$$

$$\Delta C_p = 2 C_{pB} - C_{pA} = 20 - 12 = 8 \text{ J/mol} \cdot K$$

$$\Delta H_{rx} = \Delta H_{rx}(300) + \Delta C_p(T - 300) = -75000 + 8(T - 300)$$

P9-8 cont'd

$$N_{AO} = 0.6667 * 900 * 254 = 272\,127 \text{ mol A}$$

$$N_{IO} = 0.3333 * 900 * 454 = 136\,064 \text{ mol I}$$

$$C_{AO} = N_{AO} / V = 272\,127 / (50 * 28.12) = 192 \text{ mol / dm}^3$$

$$C_{ps} = \sum \theta_i C_{pi} = \theta_A C_{pA} + \theta_B C_{pB} + \theta_I C_{pI}$$

$$= (1)(12) + 0 + (136\,064 / 272\,027) * (15) = 19.5 \text{ J/mol}$$

Energy balance :

$$T = T_o + \frac{[-\Delta H_{rx}(300).X]}{C_{pA} + \Delta C_p.X} = 300 + \frac{(-75000).X}{19.5 + 8.X}$$

⇒ POLYMATH

9-8

Equations:

$$d(x)/d(\tau) = k_1 * (1-x) - (4 * c_{ao} * (x^2) / K_e)$$

$$T_o = 300$$

$$c_{ao} = 192$$

$$T = T_o + (75000 * x) / (19.5 + (8 * x))$$

$$k_1 = 217 * \exp(1022 * (1/340 - 1/T))$$

$$\Delta H_{rx} = -75000 - (8 * (T - 300))$$

$$K_e = 70000 * \exp(\Delta H_{rx} / (8.314 * (1/300 - 1/T)))$$

$$\tau_o = 0, \quad \tau_f = 2$$

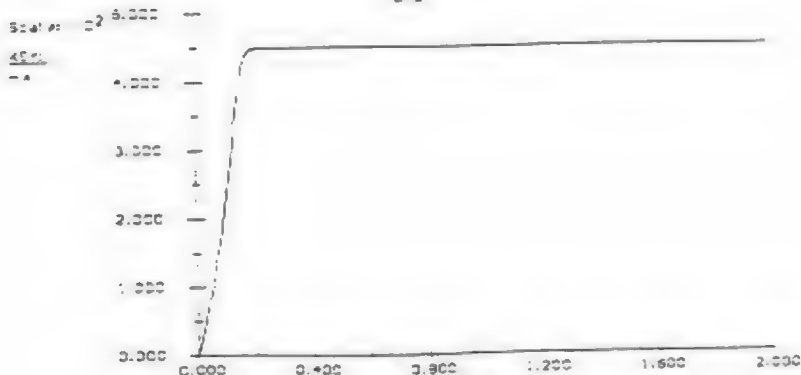
Initial value

0

9-8

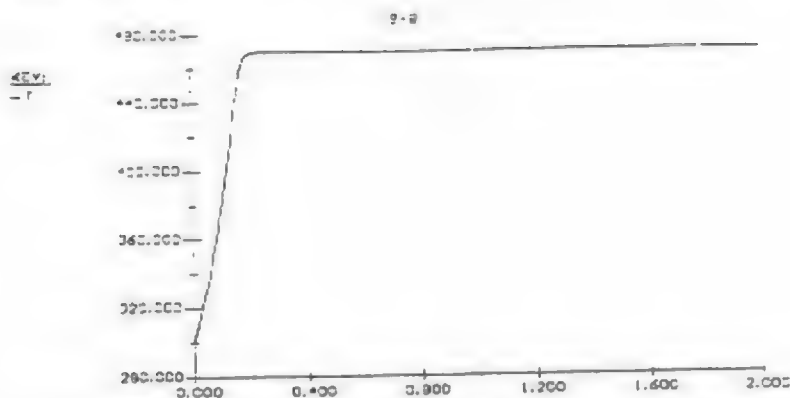
Variable	Initial value	Maximum value	Minimum value	Final value
τ	0	2	0	2
x	0	0.0449573	0	0.0449573
T_o	300	300	300	300
c_{ao}	192	192	192	192
T	300	469.781	300	469.781
k_1	0.145345	0.49785	0.145345	0.49785
ΔH_{rx}	-75000	-73641.8	-75000	-73641.8
K_e	70000	70000	1.62532	1.62532

9-8



9-22

P9-8 cont'd



Equilibrium conversion, $X_e = 4.5\%$

90 % of $X_e = 0.9 * 4.5 = 4.05\%$ conversion

Time for this conversion $\approx 0.11 \text{ min} = 6.6 \text{ s}$

Check :

at equilibrium :

$$C_{A0}(1 - X_e) = \frac{4.C_{A0}^2 X_e^2}{K_e}$$

$$(4.C_{A0}^2).X_e^2 + (K_e.C_{A0}).X_e - K_e.C_{A0} = 0$$

using the solution to a quadratic :

$$X_e = \frac{-K_e.C_{A0} \pm \sqrt{K_e^2.C_{A0}^2 - 16.K_e.C_{A0}^3}}{8.C_{A0}^2}$$

where at $T = T_e = 470 \text{ K}$, $K_e = 1.625 \text{ mol} / \text{dm}^3$

$$X_e = \frac{-(1.625 * 192) + \sqrt{(1.625)^2 (192)^2 - [16 * (1.6 * (192)^3)]}}{8 * (192)^2} = 0.045$$

From POLYMATH, $X_e = 0.045$

9-23

P9-9_B

First order liquid phase, CSTR

First solve the steady state problem for the heat exchange area A for normal operation
 $T = 358 \text{ K}$

Mol balance : $\frac{(C_{AO} - C_A)}{\tau} + r_A = \frac{dC_A}{dt} = 0$ $-\frac{C_B}{\tau} - r_A \cdot V = \frac{dC_B}{dt} = 0$

$$\text{Ln}\left(\frac{k_1}{k_2}\right) = \frac{E}{R \cdot T_2} - \frac{E}{R \cdot T_1}$$

$$E = \frac{\text{Ln}\left(\frac{k_1}{k_2}\right)}{\frac{1}{R \cdot T_2} - \frac{1}{R \cdot T_1}} = \frac{\text{Ln}\left(\frac{1.1}{3.4}\right)}{\frac{1}{8.314(323)} - \frac{1}{8.314(313)}}$$

$$94852 = \text{J/mol K}$$

$$k = 1.1 \exp\left[\frac{94852}{8.314} \left(\frac{1}{313} - \frac{1}{T}\right)\right] = 107.4 / \text{min} \quad \text{for } T = 358 \text{ K}$$

Steady state solution :

$$v_0 = \frac{F_{AO}}{C_{AO}} = \frac{90000}{90 \cdot 2} = 500 \text{ dm}^3 / \text{min}$$

$$\tau = \frac{V}{v} = \frac{200}{500} = 0.4 / \text{min}$$

$$C_{AO} = 2 \text{ M} = 2 \cdot 90 = 180 \text{ g/dm}^3$$

$$C_A = C_{AO} + r_A \cdot \tau = 180 + 0.4 r_A$$

$$C_B = -r_A \tau = -0.4 r_A$$

$$-r_A = k \cdot C_A$$

$$C_A = 180 - 107.4 (0.4) C_A$$

$$C_A = \frac{180}{1 + (0.4 \cdot 107.4)} = 4.1 \text{ g/dm}^3$$

$$r_A = -107.4 \cdot 4.1 = -440 \text{ g/min.dm}^3$$

9-24

P9-9 cont'd

$$C_B = -(-440) 0.4 = 175.9 \text{ g/dm}^3$$

Energy balance :

$$\frac{dT}{dt} = \frac{Q - W_s - \sum F_{io} C_{pi}(T - T_{io}) + (-\Delta H_{rx})(-r_a V)}{\sum N_i C_{pi}} = 0$$

$$Q = UA(T_a - T) = (120 \times 60)A(273 - T) \quad \text{J/min}$$

$$F_{AO} C_{pA} (T - T_{AO}) = 90000 \times 2 \times (T - 313) \quad \text{J/min}$$

$$A = \frac{-180000.(358 - 313) + (250)(440 \times 200)}{7200(273 - 358)} = 22.7 \text{ m}^2$$

Use the unsteady state equations to determine what heat exchange area A will give a runaway reaction.

where $\sum N_i C_{pi} = C_{p\text{tot}} \rho_{\text{tot}} V = 2 \times 900 \times 200 = 360000 \text{ J/K}$

The POLYMATH results for $A = 22.6 \text{ m}^2$ are given

Problem P9-9b

Equations:

$$\begin{aligned} d(ca)/d(t) &= ((180-ca)/\tau) + (ra) & \text{Initial value} \\ d(cb)/d(t) &= -ra - (cb/\tau) & 180 \\ d(T)/d(t) &= ((7200 \times \lambda \times (273-T)) - (90000 \times 2 \times (T-313)) + ((1-250) \times ra \times 313) & 0 \\ & V) / (2 \times 900 \times 200) & 313 \end{aligned}$$

$$\tau = 0.4$$

$$A = 22.696$$

$$k = 1.1 \times \exp(11409 \times ((1/313) - (1/T)))$$

$$V = 200$$

$$ra = k \times ca$$

$$Na = ca/V$$

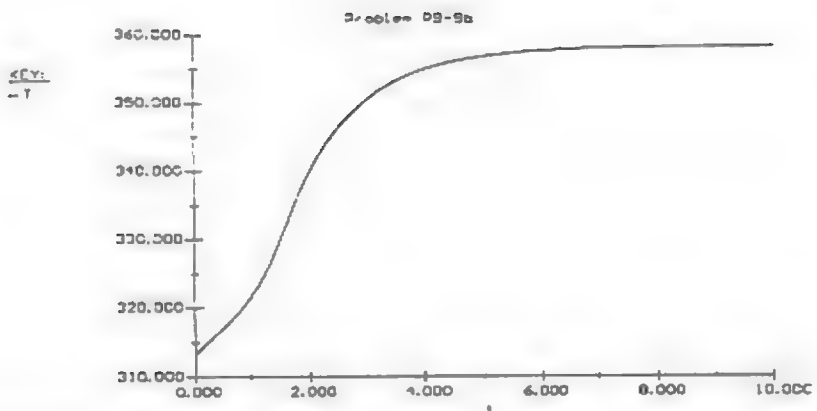
$$Nb = cb/V$$

$$t_0 = 0, \quad t_f = 10$$

Problem P9-9b

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	10	0	10
ca	180	180	4.10076	4.10076
cb	0	175.899	0	175.899
T	313	357.977	313	357.977
tau	0.4	0.4	0.4	0.4
A	22.696	22.696	22.696	22.696
k	1.1	107.237	1.1	107.237
V	200	200	200	200
ra	-198	-197.967	-439.754	-439.754
Na	0.9	0.9	0.0205038	0.0205038
Nb	0	0.879496	0	0.879496

P9-9 cont'd



A sensitivity analysis for different values of A show that a new steady state is reached at every new A but at an increasingly higher T . The required A depends on the definition of reactor runaway.

P9-10_a

CSTR startup

Part (a) CSTR startup, gas phase, isobaric - no pressure drop

Mol balance :

$$\frac{dF_a}{dt} = (F_{a0} - F_a) + r_a V$$

$$\frac{dF_b}{dt} = (0 - F_b) - 2r_a V$$

$$C_a = \frac{F_a}{v_r}$$

$$C_b = \frac{F_b}{v_r}$$

$$v_r = v_a + v_b$$

$$F_r = C_r v_r = \frac{P}{R \cdot T} \cdot v_r$$

$$F_{T0} = C_{T0} v_{T0} = \frac{P}{R \cdot T_0} \cdot v_{T0}$$

$$v_r = v_{T0} \frac{F_r}{F_{T0}} \cdot \frac{T}{T_0}$$

$$F_r = F_a + F_b$$

$$F_{T0} = F_{a0} + F_{b0}$$

9-26

P9-10 cont'd

$$V = v_T \tau$$

$$\tau = 500 \text{ s}$$

Energy balance :

$$\frac{dT}{dt} = \frac{Q - \sum F_{i0} C_{pi} (T - T_{i0}) + (-\Delta H_{rx})(-r_a V)}{\sum N_i C_{pi}}$$

$$\frac{UA}{\rho_{cat}} = 5 \text{ J / kg cat.s.K}$$

but kg catalyst = 50 kg

$$UA = 5 \times 50 = 250 \text{ J / s.K}$$

$$\Delta C_p = 0$$

$$\frac{dT}{dt} = \frac{250.(T_a - T) - 40.F_{a0}.(T - T_{i0}) + 20000.(-r_a V)}{40.C_a V + 20.C_b V}$$

No control :

$$T_a = 300 \text{ K}, T_{i0} = 450 \text{ K}, F_{a0} = 5 \text{ mol/s}$$

Problem P9-13B(A)

Equations:

$$d(fa)/d(\tau) = (f_{a0} - fa) - (r_a \cdot V)$$

Initial value

$$d(fb)/d(\tau) = (-fa) - (2 \cdot r_a \cdot V)$$

1e-08

$$d(T)/d(\tau) = ((250 \cdot (T_a - T)) - (40 \cdot f_{a0} \cdot (T - T_{i0})) + (20000 \cdot (-r_a \cdot V))) / (40 \cdot C_a \cdot V + 20 \cdot C_b \cdot V)$$

0

$$f_{a0} = 5$$

$$T_a = 300$$

$$T_{i0} = 450$$

$$f_{i0} = f_{a0} - f_b$$

$$T_0 = 450$$

$$\tau_{au} = 500$$

$$\tau_{bu} = 500$$

$$k = \exp((31400/8.314) \cdot ((1/450) - (1/T)))$$

$$C_{a0} = 0.25$$

$$f_{i0} = f_{a0}$$

$$v_0 = f_{a0}/C_{a0}$$

$$v = v_0 \cdot f_{i0} \cdot T / (f_{i0} \cdot T_0)$$

$$C_a = f_a/v$$

$$C_b = f_b/v$$

$$V = v \cdot \tau_{au}$$

$$r_a = -k \cdot C_a$$

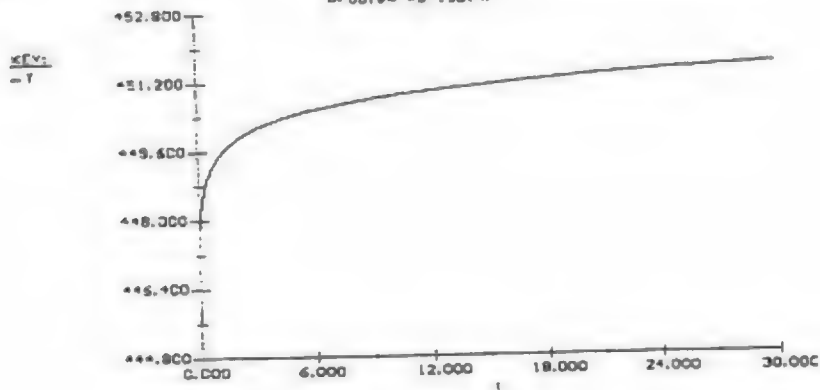
$$\tau_0 = 0, \quad \tau_f = 30$$

P9-10 cont'd

Problem P9-13B(A)

Variable	Initial value	Maximum value	Minimum value	Final value
τ	0	30	0	30
f_a	1e-08	0.0106221	1e-08	0.00969749
f_b	0	299.098	0	299.098
T	450	451.548	445.634	451.548
f_{ao}	5	5	5	5
T_a	300	300	300	300
T_{io}	450	450	450	450
f_c	1e-08	299.107	1e-08	299.107
T_o	450	450	450	450
τ_{au}	500	500	500	500
τ_{au}	500	500	500	500
k	1	1.0292	0.921054	1.0292
C_{ao}	0.25	0.25	0.25	0.25
f_{to}	5	5	5	5
v_o	20	20	20	20
v	4e-08	1200.55	4e-08	1200.55
C_a	0.25	0.251187	8.07756e-06	8.07756e-06
C_b	0	0.250078	0	0.249135
v	2e-05	600273	2e-05	600273
r_a	-0.25	-8.31339e-06	-0.25	-8.31339e-06

Problem P9-13B(A)



Part (b)

Mol balance :

$$\frac{dC_a}{dt} = \frac{(C_{ao} - C_a)}{\tau} + r_a$$

$$C_{ao} = 0.1 \text{ kmol/m}^3 = 0.1 \text{ mol/l}$$

P9-10 cont'd

$$\frac{dCb}{dt} = \frac{(Cbo - Cb)}{\tau} + ra$$

$$Cbo = Cao$$

$$\frac{dCc}{dt} = \frac{(0 - Cc)}{\tau} - ra$$

$$\tau = 50 \text{ s}$$

Rate law :

$$-ra = k.Ca.Cb$$

$$k(T) = 0.01 \exp \left[\frac{10000}{1.987} \left(\frac{1}{300} - \frac{1}{T} \right) \right]$$

Energy balance :

$$\frac{dT}{dt} = \frac{Q - Ws - \sum F_{io}.C_{pi}(T - T_{io}) + (-\Delta H_{rx})(-ra.V)}{\sum N_i.C_{pi}}$$

$$V = v_o . \tau = 2 \times 50 = 100 \text{ dm}^3$$

$$F_{ao} = C_{ao} . v_o = 0.1 \times 2 = 0.2 \text{ mol/s} = F_{bo} \text{ (equimolar feed)}$$

$$\sum F_{io}.C_{pi}.(T - T_{io}) = 2 \times 0.2 \times (15)(T - 300) = 6(T - 300)$$

$$\begin{aligned} \Delta H_{rx}(T) &= \Delta H_{rx}(T_o) + \Delta C_p.(T - T_o) && \text{but } \Delta C_p = 0 \\ &= -41000 - (-20000) - (-15000) \\ &= -6000 \text{ cal/mol} \end{aligned}$$

$$\frac{dT}{dt} = \frac{6(T - 300) + (6000).(-ra.V)}{15.Ca.v + 15.Cb.V + 30.Cc.V}$$

Problem P9-10B(B)

Equations:

$$d(ca)/d(t) = ((0.1 - ca)/50) + ra$$

$$d(cb)/d(t) = ((0.1 - cb)/50) + ra$$

$$d(cc)/d(t) = ((0 - cc)/50) - ra$$

$$d(T)/d(t) = ((6 \cdot (T - 300)) - (6000 \cdot (-ra \cdot V))) / ((15 \cdot ca \cdot V) + (15 \cdot cb \cdot V) + (30 \cdot cc \cdot V))$$

$$V = 100$$

$$k = 0.01 \cdot \exp \left(\frac{10000}{1.987} \cdot \left(\frac{1}{300} - \frac{1}{T} \right) \right)$$

$$ra = -k \cdot ca \cdot cb$$

$$t_0 = 0, \quad t_f = 400$$

Initial value

$$0.001$$

$$0.002$$

$$0$$

$$300$$

P9-10 cont'd

Problem P9-10B(3)

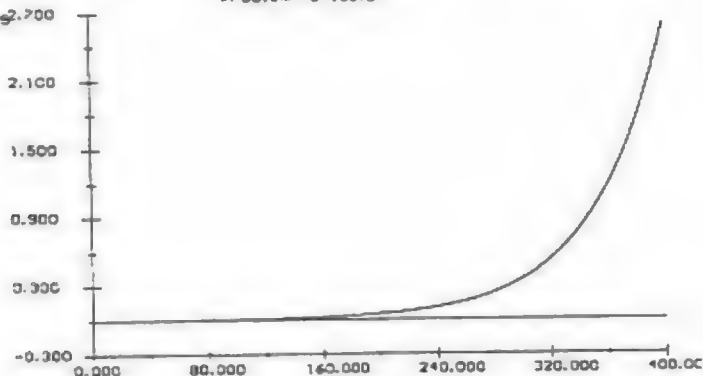
Variable	Initial value	Maximum value	Minimum value	Final value
c	0	400	0	400
ca	0.001	0.0732615	0.00010274	0.00010274
cb	0.001	0.0732615	0.00010274	0.00010274
cc	0	0.099864	0	0.099864
T	300	257380	300	257380
V	100	100	100	100
k	0.01	189280	0.01	189280
ra	-1e-08	-1e-08	-0.0110871	-0.00199796

Problem P9-10B(3)

Scale: 10^{-5} 2.700

KEY:

-T

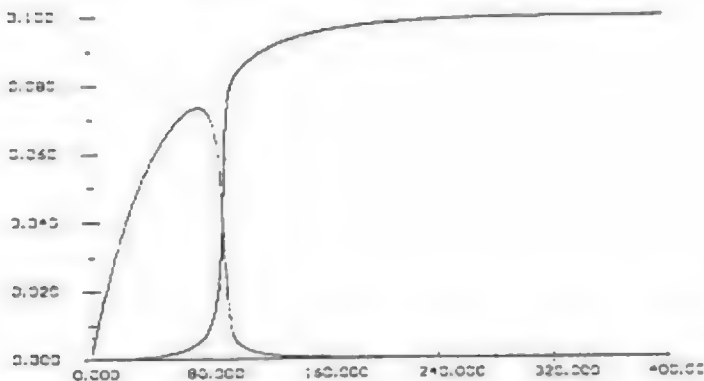


KEY:

-ca

cb

-cc



P9-11g

Semibatch problem

Part (a)

Mol balance : $\frac{dN_a}{dt} = raV$ $N_{a0} \frac{dX}{dt} = -raV$

$$\frac{dN_b}{dt} = 2.ra.V + F_{b0} \quad F_{b0} = C_{b0}.v_o = 4.v_o$$

$$\frac{dN_c}{dt} = -raV \quad V = V_o + v_o.t$$

Rate law : $-ra = k.C_a.C_b^2$

$$k(T) = 0.0005 \exp \left[\frac{8000}{1.987} \left(\frac{1}{300} - \frac{1}{T} \right) \right]$$

Stoichiometry : $C_a = \frac{N_a}{V}$ $C_b = \frac{N_b}{V}$ $C_c = \frac{N_c}{V}$

Energy balance :

$$\frac{dT}{dt} = \frac{Q - W_s - \sum F_{i0}.C_{pi}.(T - T_{i0}) + (-\Delta H_{rx}(T)).(-ra.V)}{\sum N_i.C_{pi}}$$

where $Q = UA.(T_a - T) = 250.(390 - T)$

$$W_s = 0$$

$$\Delta H_{rx}(T) = -55000$$

$$\sum F_{i0}.C_{pi} = F_{b0}.C_{pb} = C_{b0}.v_o.C_{pb} = 4.v_o \cdot 20 = 80v_o$$

$$\sum N_i.C_{pi} = N_a C_{pa} + N_b.C_{pb} + N_c.C_{pc} = 35N_a + 20N_b + 75N_c$$

$$\frac{dT}{dt} = \frac{250.(290 - T) - 80.v_o.(T - 325) + (-55000).(-ra.V)}{35.N_a + 20.N_b + 75.N_c}$$

9-31

P9-11 cont'd

9-11

Equations:

$$d(na)/dt = ra \cdot V$$

$$d(X)/dt = (-ra \cdot V/50)$$

$$d(nb)/dt = (2 \cdot ra \cdot V) + fbo$$

$$d(nc)/dt = -ra \cdot V$$

$$d(T)/dt = ((250 \cdot (290 - T)) - (80 \cdot vb \cdot (T - 325)) + (-55000 \cdot (-ra \cdot V))) / ((35 \cdot na) + (20 \cdot nb) + (75 \cdot nc))$$

$$vb = 1.5$$

$$k = 0.0005 \cdot \exp((8000/1.987) \cdot ((1/300) - (1/T)))$$

$$V = 10 \cdot (vb \cdot t)$$

$$fbo = 4 \cdot vb$$

$$ca = na/V$$

$$cb = nb/V$$

$$cc = nc/V$$

$$ra = -k \cdot ca \cdot (cb^2)$$

$$t_0 = 0, \quad t_f = 1000$$

Initial value

50

0

0

0

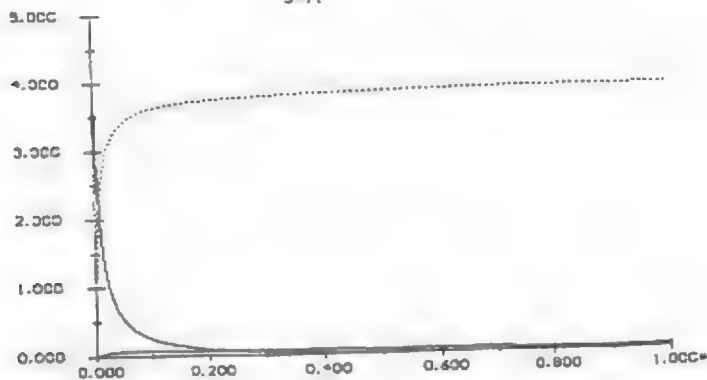
300

9-11

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	1000	0	1000
na	50	50	0.332447	0.332447
X	0	0.993351	0	0.993351
nb	0	5900.66	0	5900.66
nc	0	49.6676	0	49.6676
T	300	300.182	283.593	298.764
vb	1.5	1.5	1.5	1.5
k	0.0005	0.000504079	0.000230027	0.000472992
V	10	1510	10	1510
fbo	6	6	6	6
ca	5	5	0.000220164	0.000220164
cb	0	3.90773	0	3.90773
cc	0	0.0718812	0	0.0328924
ra	-0	-0	-0.00411466	-1.59018e-06

9-11

Legend:
- ca
- cb
- cc



9-32

P9-11 cont'd

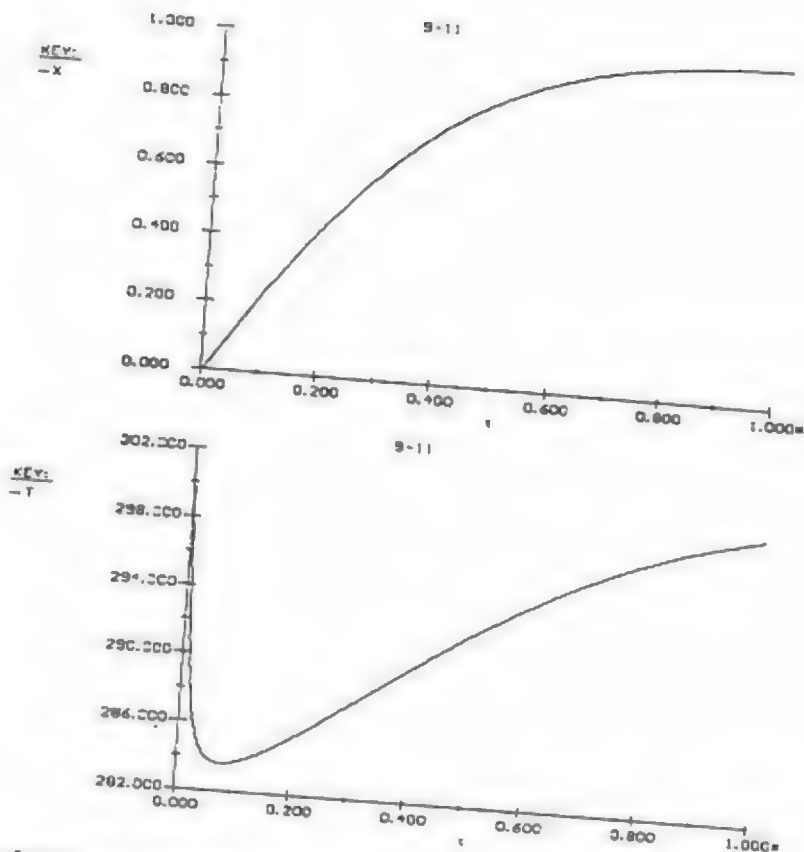


Table 1. Iterating wrt v_0 for $X=0.8$ and $T<403K$ and daily $N_c = 120 \text{ mol C}$

v_0 dm^3/min	T ($X=0.8$) K	t ($X=0.8$) min	N_c ($X=0.8$) mol	Daily N_c $N_c(24 \cdot 60/t + 30)$ mol
1	289	521	40	104
5	300	262	40	197
2	293	400	40	134
1.5	291	450	40	120

A flowrate of 1.5 mol B/min would produce 120 mol C/ day , with $X = 80 \%$ and $T < 130^\circ\text{C}$ at all times.

P9-11 cont'd

Part (b)

If the max. coolant rate falls to 200 mol/min, then it may not be prudent to assume that the coolant leaves at the entering ambient temperature, T_a . It should be assumed that the coolant temperature varies spatially along the heat exchanger pipes and the required term for the heat exchange would be :

$$Q = m_c C_{p_{cool}} (T_{a1} - T_{a2}) \quad \text{where } T_{a1} = \text{ambient } T \text{ coolant entering} \\ T_{a2} = \text{ambient } T \text{ coolant leaving}$$

$$T_{a2} = T - (T - T_{a1}) \cdot \exp\left(-\frac{UA}{m_c C_{p_{cool}}}\right)$$

The reduced flowrate and hence heat exchange, may increase the reactor temperature to approaching 130°C , the upper limit, at conversions approaching 80 %, and so more caution is required. The incorporation of temperature control would be prudent.

P9-12a

CSTR startup

Need steady-state values at $T_o = 75^\circ\text{F}$

$$\text{Mol balance : } \frac{dN_a}{dt} = F_{a0} - F_a + r_a \cdot V$$

$$\frac{dC_a}{dt} = \frac{(C_{a0} - C_a) \cdot v_0}{V} + r_a$$

$$\frac{dC_b}{dt} = \frac{(C_{b0} - C_b) \cdot v_0}{V} + r_a$$

$$\frac{dC_c}{dt} = \frac{(C_{c0} - C_c) \cdot v_0}{V} - r_a$$

$$\frac{dC_M}{dt} = \frac{(C_{M0} - C_M) \cdot v_0}{V}$$

P9-12 cont'd

$$C_{io} = \frac{F_{io}}{v_o}$$

$$C_{ao} = \frac{F_{ao}}{v_o} = 0.18157 \text{ lb mol/ft}^3$$

$$C_{bo} = \frac{F_{bo}}{v_o} = 2.2696 \text{ lb mol/ft}^3$$

$$C_{co} = 0$$

$$C_{mo} = \frac{F_{mo}}{v_o} = 0.22696 \text{ lb mol/ft}^3$$

$$V = \frac{1}{7.484} \times 500$$

$$v_o = \frac{F_{ao}}{\rho_{ao}} + \frac{F_{bo}}{\rho_{bo}} + \frac{F_{mo}}{\rho_{mo}} = \frac{80}{0.932} + \frac{1000}{3.45} + \frac{100}{1.54} = 440.6 \text{ ft}^3/\text{hr}$$

Rate law : $-r_a = k.C_a$ (Cb in excess)

$$k = 16.96 \times 10^{12} \cdot \exp\left(-\frac{32400}{1987(T + 460)}\right)$$

Energy balance :

$$\frac{dT}{dt} = \frac{Q - W_s - \sum F_{io}.C_{pi}(T - T_{io}) + (-\Delta H_{rx})(-r_a.V)}{\sum N_i.C_{pi}}$$

$$W_s = 0$$

$$Q = m_c.C_{pcool}.(T_{a1} - T_{a2}) = 1000 \times 18 \times (60 - T_{a2})$$

$$\sum F_{io}.C_{pi}.(T - T_{io}) = [F_{ao}.C_{pa} + F_{bo}.C_{pb} + F_{mo}.C_{pm}].(T - 75)$$

$$\Delta H_{rx} = -36000 \text{ Btu/lb mol}$$

$$\sum N_i.C_{pi} = N_a.C_{pa} + N_b.C_{pb} + N_c.C_{pc} + N_M.C_{pM}$$

$$= 53C_a.V + 18C_b.V + 46C_c.V + 19.5C_M.V$$

9-35

P9-12 cont'd

$$T_{a2} = T - (T - T_{a1}) \cdot \exp\left(-\frac{UA}{m_c C_{p_{cool}}}\right)$$

$$= T - (T - 60) \cdot \exp\left(-\frac{16000}{1000 \times 18}\right)$$

$$= T - 0.41111(T - 60)$$

$$\frac{dT}{dt} = \frac{18000(60 - (T - 0.41111(T - 60)) - 22750(T - 75) + (36000)(-r_a.V)}{35C_a.V + 18C_b.V + 46C_c.V + 19.5C_M.V}$$

\Rightarrow POLYMATH

Initial conditions : $T_o = 75$, $T = 138.5$ °F, $C_a = 0.03780$, $C_b = 3.3062$,
 $C_c = 0.0144$, $C_M = 0.2269$ lb mol / ft³

If T_o drops from 75 to 70 °F

Part (a)

P-control only : manipulated variable = m_c

controlled variable = T

$$m_c = m_{co} + k_c.(T - T_{sp})$$

$$\begin{aligned} \text{where } m_{co} &= 1000 \text{ lb mol/h} \\ T_{sp} &= 138.5 \text{ °F} \\ k_c &= 10 \end{aligned}$$

P9-12 cont'd

P9-12 (a)

Equations:

	<u>Initial value</u>
$d(Ca)/dt = (((Ca_0 - Ca) \cdot vo)/V) + ra$	0.0378
$d(Cb)/dt = (((3.45 - Cb) \cdot vo)/V) + ra$	3.3062
$d(Cc)/dt = (((0 - Cc) \cdot vo)/V) - ra$	0.0144
$d(Cm)/dt = (((C_{m0} - C_m) \cdot vo)/V)$	0.2269
$d(T)/dt = ((mc \cdot 18 \cdot (60 - (T - (0.41111 \cdot (T - 60)))) - (22750 \cdot (T - T_0))) / ((36000 \cdot (-ra \cdot V)) / ((35 \cdot Ca \cdot V) + (46 \cdot Cb \cdot V) + (19.5 \cdot C_m \cdot V) + (18 \cdot Cb \cdot V)))$	138.5

$Ca_0 = 0.18157$

$vo = 440.6$

$V = (1/7.484) \cdot 500$

$C_{m0} = 0.22696$

$k = 16.96 \cdot 12 \cdot \exp(-32400 / (1.987 \cdot (T + 460)))$

$Cb_0 = 2.2696$

$T_0 = 70$

$mco = 1000$

$kc = 10$

$Tsp = 138.5$

$ra = -k \cdot Ca$

$mc = mco \cdot (kc \cdot (T - Tsp))$

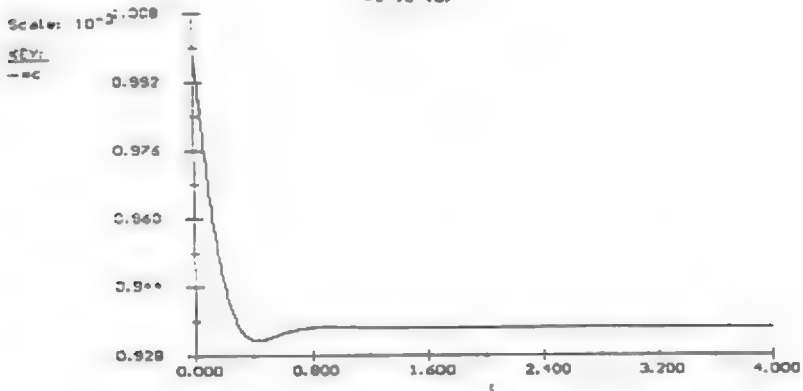
$t_0 = 0 \quad t_f = 4$

P9-12 (a)

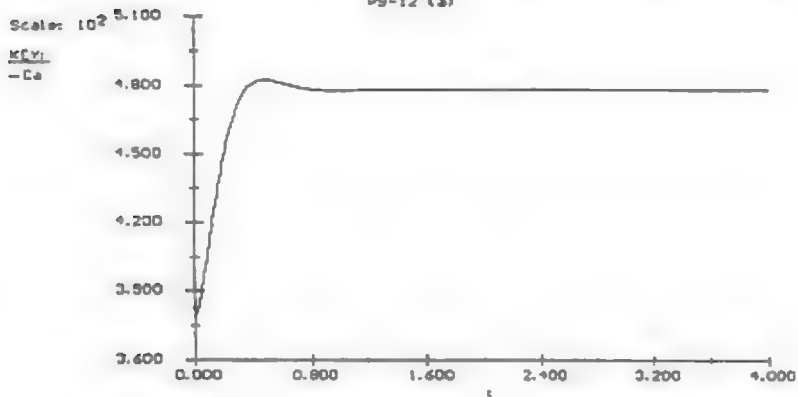
<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
t	0	4	0	4
Ca	0.0378	0.0482444	0.0378	0.0478056
Cb	3.3062	3.31667	3.3062	3.31624
Cc	0.0144	0.133764	0.0144	0.133764
Cm	0.2269	0.22696	0.2269	0.22696
T	138.5	138.5	131.65	131.941
Ca0	0.18157	0.18157	0.18157	0.18157
vo	440.6	440.6	440.6	440.6
V	66.8092	66.8092	66.8092	66.8092
Cm0	0.22696	0.22696	0.22696	0.22696
k	24.9561	24.9561	18.2047	18.4531
Cb0	2.2696	2.2696	2.2696	2.2696
To	70	70	70	70
mco	1000	1000	1000	1000,
kc	10	10	10	10
Tsp	138.5	138.5	138.5	138.5
ra	-0.943341	-0.870142	-0.943341	-0.882163
mc	1000	1000	931.499	934.41

P2-12 cont'd

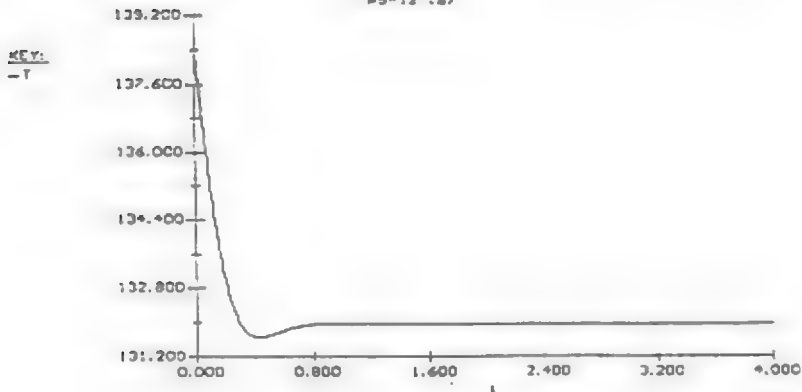
P2-12 (a)



P2-12 (a)



P2-12 (a)



P9-12 cont'd

Part (b)

I-control only :

manipulated variable = m_c

controlled variable = T

$$m_c = m_{co} + \frac{kc}{u} I$$

where $m_{co} = 1000 \text{ lb mol/h}$

$kc = 10, \tau_i = 1$

$$\frac{dT}{dt} = (T - T_{sp})$$

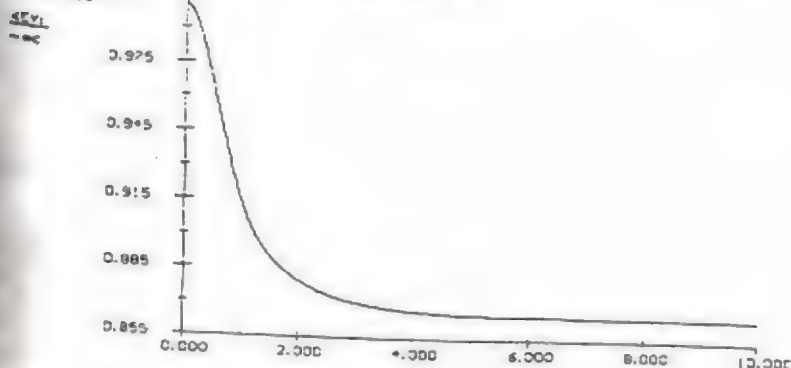
$T_{sp} = 138.5^\circ\text{F}$

Problem P9-12B

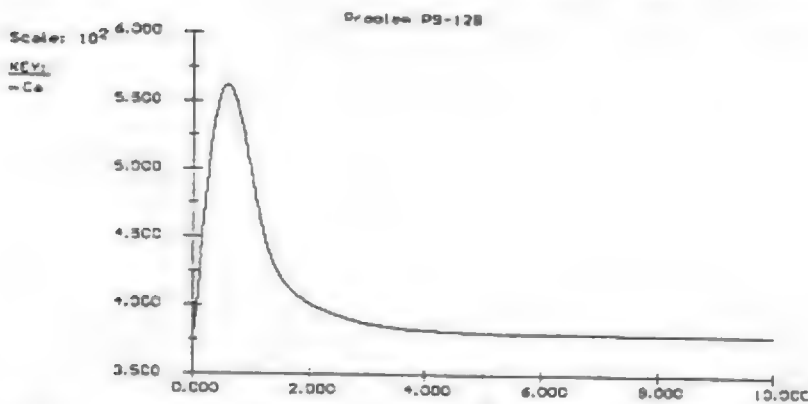
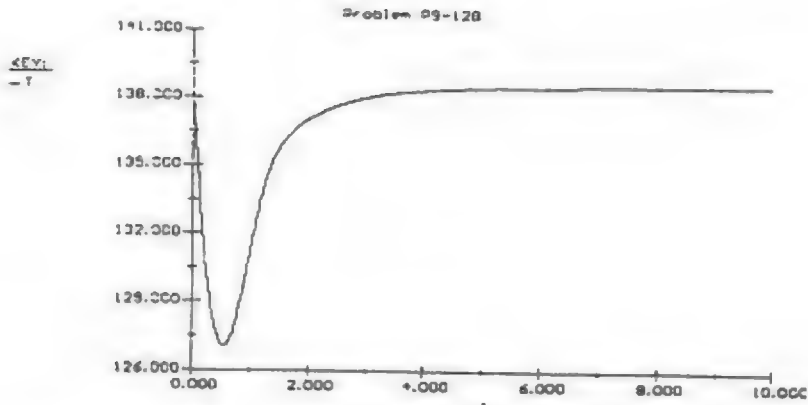
Variable	Initial value	Maximum value	Minimum value	Final value
t	0	10	0	10
Ca	0.0378	0.0561803	0.0378	0.0379531
Cb	3.3062	3.32461	3.3062	3.30638
Cc	0.0144	0.143617	0.0144	0.143617
Ca	0.2269	0.22696	0.2269	0.22696
T	138.5	138.5	127.056	138.499
I	0	0	-13.516	-13.516
Ca0	0.18157	0.18157	0.18157	0.18157
vo	440.6	440.6	440.6	440.6
v	66.8092	66.8092	66.8092	66.8092
Cao	0.22696	0.22696	0.22696	0.22696
To	70	70	70	70
Tsp	138.5	138.5	138.5	138.5
k	24.9561	24.9561	14.6734	24.9555
Cbo	2.2696	2.2696	2.2696	2.2696
mco	1000	1000	1000	1000
kc	10	10	10	10
tauI	1	1	1	1
ra	-0.943341	-0.818007	-0.94714	-0.94714
mc	1000	1000	864.84	864.84

Scale: 10-3.005

Problem P9-12B



P9-12 cont'd



Part (c)

PI-control only : manipulated variable = m_c

controlled variable = T

$$m_c = m_{c0} + kc(T - T_{sp}) + \frac{kc}{\tau_I} I \quad \text{where } m_{c0} = 1000 \text{ lb mol/h}$$

$$kc = 10, \tau_I = 1$$

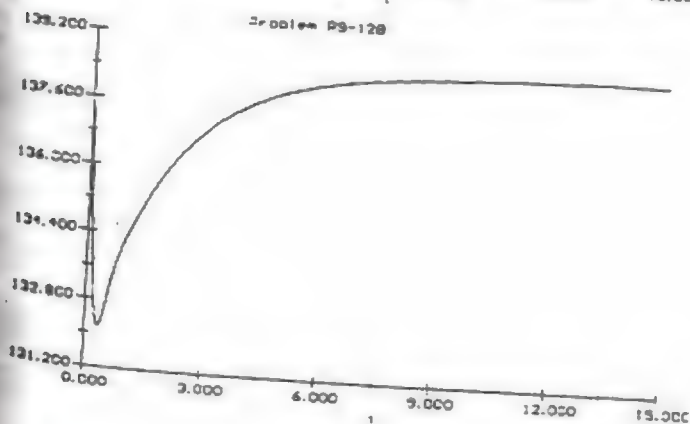
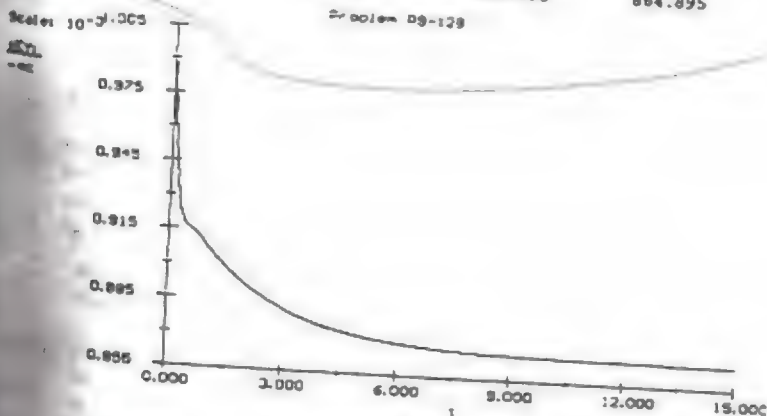
$$\frac{dI}{dt} = (T - T_{sp})$$

$$T_{sp} = 138.5 \text{ } ^\circ\text{F}$$

P9-12 cont'd

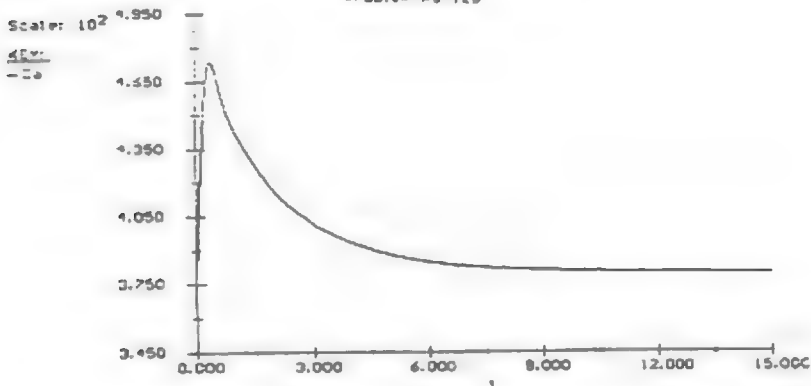
Problem P9-12B

Variable	Initial value	Maximum value	Minimum value	Final value
E	0	15	0	15
Ca	0.0378	0.0473519	0.0378	0.0379598
Cb	3.3062	3.31578	3.3062	3.30639
Cc	0.0144	0.14361	0.0144	0.14361
Cd	0.2269	0.22696	0.2269	0.22696
T	138.5	138.5	132.165	138.495
I	0	0	-13.5052	-13.5052
Cao	0.18157	0.18157	0.18157	0.18157
vo	440.6	440.6	440.6	440.6
v	66.8092	66.8092	66.8092	66.8092
Cho	0.22696	0.22696	0.22696	0.22696
To	70	70	70	70
Tsp	138.5	138.5	138.5	138.5
k	24.9561	24.9561	18.6468	24.95
Cho	2.2696	2.2696	2.2696	2.2696
aco	1000	1000	1000	1000
ko	10	10	10	10
tauI	1	1	1	1
ra	-0.943341	-0.872788	-0.947099	-0.947099
rc	1000	1000	864.895	864.895



P9-12 cont'd

Problem P9-12a



P9-13a

CSTR startup

Part (b)

Mol balance : $\frac{dC_A}{dt} = \frac{(C_{Ao} - C_A)}{\tau} + r_A$ $C_{Ao} = 0.1$

kmol/m^3 $= 0.1$

mol/dm^3

$\frac{dC_B}{dt} = \frac{(C_{Bo} - C_B)}{\tau} + r_A$ $C_{Bo} = C_{Ao}$

$\frac{dC_C}{dt} = \frac{(0 - C_C)}{\tau} - r_A$ $\tau = 50 \text{ s}$

Rate law : $-r_A = k C_A C_B$

$k(T) = 0.01 \exp \left[\frac{10000}{1.987} \left(\frac{1}{300} - \frac{1}{T} \right) \right]$

Energy balance : $\frac{dT}{dt} = \frac{Q - W_s - \sum F_{iO} C_{pi} (T - T_{iO}) + (-\Delta H_{rx}) (-r_A V)}{\sum N_i C_{pi}}$

9-42

P9-13 cont'd

$$V = v_o \cdot \tau = 2 \times 50 = 100 \text{ dm}^3$$

$$F_{ao} = C_{ao} \cdot v_o = 0.1 \times 2 = 0.2 \text{ mol/s} = F_{bo} \text{ (equimolar feed)}$$

$$\Sigma F_{io} \cdot C_{pi} \cdot (T - T_{io}) = 2 \times 0.2 \times (15)(T - 300) = 6(T - 300)$$

$$\begin{aligned} \Delta H_{rx}(T) &= \Delta H_{rx}(T_o) + \Delta C_p \cdot (T - T_o) && \text{but } \Delta C_p = 0 \\ &= -41000 - (-20000) - (-15000) \\ &= -6000 \text{ cal/mol} \end{aligned}$$

$$\frac{dT}{dt} = \frac{6(T - 300) + (6000) \cdot (-r_a \cdot V)}{15 \cdot C_a \cdot v + 15 \cdot C_b \cdot V + 30 \cdot C_c \cdot V}$$

No control :

P9-13 (b)1

Equations:

	<u>Initial value</u>
$d(C_a)/d(t) = ((0.1 - C_a)/50) + r_a$	0.001
$d(C_b)/d(t) = ((0.1 - C_b)/50) + r_a$	0.001
$d(C_c)/d(t) = ((0 - C_c)/50) - r_a$	0
$d(T)/d(t) = ((6 \cdot (T - 300)) + (6000 \cdot (-r_a \cdot V))) / ((15 \cdot C_a \cdot v) + (15 \cdot C_b \cdot V) + (30 \cdot C_c \cdot V))$	300

$$V = 100$$

$$k = 0.01 \cdot \exp((10000/1.987) \cdot ((1/300) - (1/T)))$$

$$r_a = -k \cdot C_a \cdot C_b$$

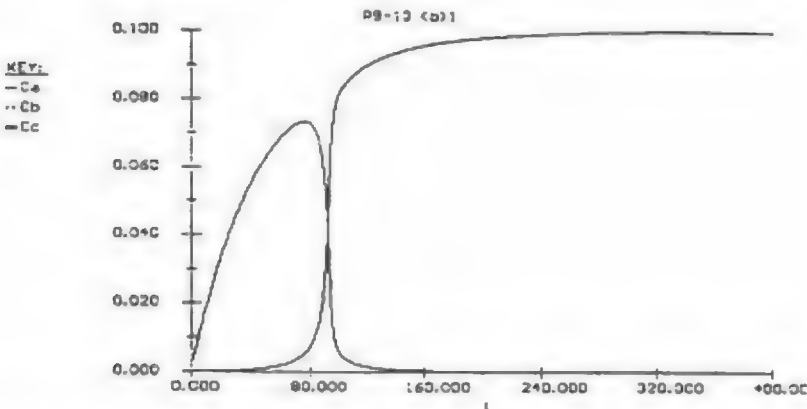
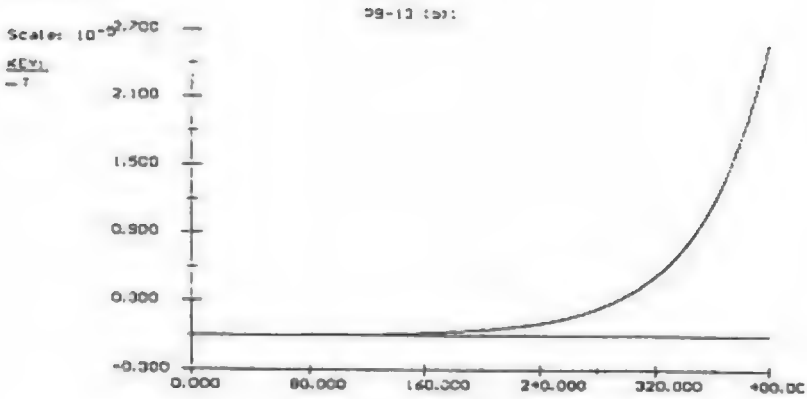
$$t_0 = 0, \quad t_f = 400$$

P9-13 (b)1

<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
t	0	400	0	400
C _a	0.001	0.0732615	0.00010274	0.00010274
C _b	0.001	0.0732615	0.00010274	0.00010274
C _c	0	0.099864	0	0.099864
T	300	257380	300	257380
V	100	100	100	100
k	0.01	189280	0.01	189280
r _a	-1e-08	-1e-08	-0.0110871	-0.00199796

9-43

P9-13 cont'd



The results without control, indicate a runaway reaction, as T continues to increase after the concentrations have approached their steady-state values

Control aspects : assume that the operating T should not exceed 550K, the boiling point of the liquid.

Without given data for heat exchange :

Try manipulated variable = T_{i0} (inlet feed T)
controlled variable = T

P-control : $T_{i0} = \text{IF } (T < 550) \text{ THEN } (300) \text{ ELSE } (T_{i00} + k_c \cdot (T - T_{sp}))$

where $T_{sp} = 550 \text{ K}$, $T_{i00} = 300 \text{ K}$, $k_c = -10$

\Rightarrow T_{i0} manipulation not feasible for T control for any k_c (requires $T_{i0} \sim -2000 \text{ K}$)

P9-13 cont'd

P9-13 (b) 2

Equations:

$$d(Ca)/dt = ((0.1 - Ca)/\tau) + r_a$$

$$d(Cb)/dt = ((0.1 - Cb)/\tau) + r_a$$

$$d(Cc)/dt = ((0 - Cc)/\tau) - r_a$$

$$d(T)/dt = ((-2 \cdot P_{ao} \cdot (T - T_{io})) + (6000 \cdot (-r_a \cdot V))) / ((15 \cdot Ca \cdot V) + (1 \cdot 300 \cdot Cb \cdot V) + (30 \cdot Cc \cdot V))$$

Initial value

0.0001

0.0001

0

300

$$\tau = 50$$

$$k = 0.01 \cdot \exp((10000/1.987) \cdot ((1/300) - (1/T)))$$

$$k_c = 10$$

$$T_{sp} = 550$$

$$v_o = 2$$

$$T_{io} = 300$$

$$r_a = -k \cdot Ca \cdot Cb$$

$$P_{ao} = 0.1 \cdot v_o$$

$$V = \tau \cdot v_o$$

$$T_{io} = \text{if}(T < 550) \text{ then}(T_{io}) \text{ else}(T_{io} + (k_c \cdot (T - T_{sp})))$$

$$t_0 = 0, \quad t_f = 400$$

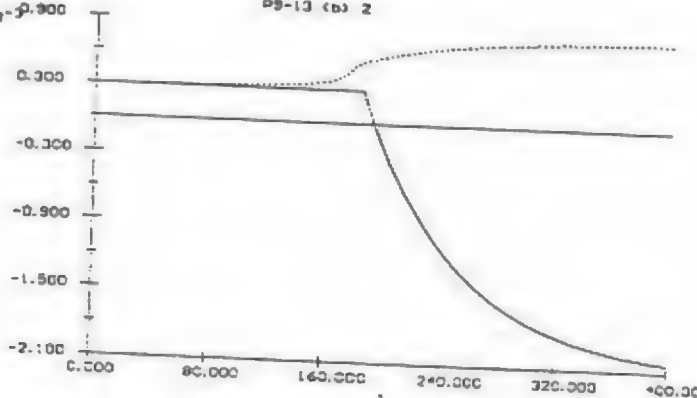
Scale: 10^{-3} 0.300

KFV:

-Tio

..T

P9-13 (b) 2



Try

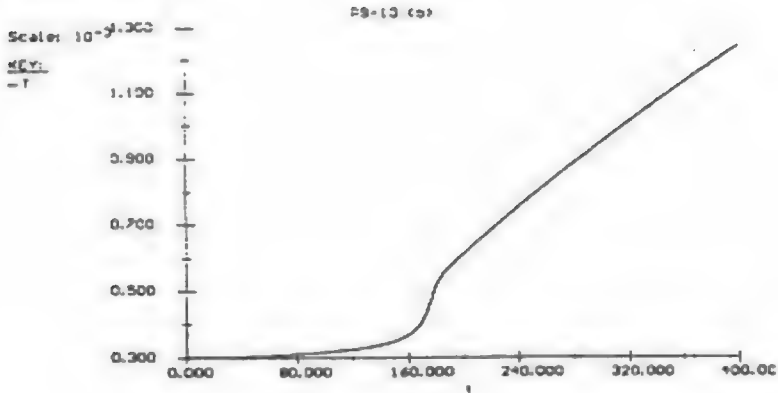
manipulated variable = v_o (inlet volumetric flowrate)
controlled variable = T

P-control : $v_o = \text{IF}(T < 550) \text{ THEN } (2) \text{ ELSE } (v_{oo} + k_c \cdot (T - T_{sp}))$

where $T_{sp} = 550 \text{ K}$, $v_{oo} = 2 \text{ dm}^3$, $k_c = 10$

$\Rightarrow T$ insensitive to v_o for any k_c

P9-13 cont'd



It is concluded that the addition of I-action will not improve control and that the only feasible control strategy is to add a heat exchange device, and to manipulate the coolant flowrate for T control.

P9-14_B

CSTR startup

Initial conditions : $T_0 = 75$, $T = 138.5^\circ\text{F}$, $C_a = 0.03780$, $C_b = 2.12$,
 $C_c = 0.0144$, $C_M = 0.2269 \text{ lb mol / ft}^3$

Part (a)

If T drops from 138.5 to 133.5°F

As in P9-12_B except :

$$\frac{dC_a}{dt} = \frac{F_{a0} - C_a \cdot v_0}{V} + r_a$$

$$v_0 = \frac{F_{a0}}{0.932} + \frac{1000}{3.45} + \frac{100}{1.54}$$

$$\frac{dT}{dt} = \frac{18000(60 - (T - 0.41111(T - 60) - (35F_{a0} + 19950) \cdot (T - 75) + (36000)(-r_a \cdot V))}{35C_a \cdot V + 18C_b \cdot V + 46C_c \cdot V + 19.5C_M \cdot V}$$

I-control only : manipulated variable = F_{a0}

P9-14 cont'd

controlled variable = T

$$F_{ao} = F_{aoo} + \frac{kc}{u} I \quad \text{where } F_{aoo} = 80 \text{ lb mol/h,}$$

say $kc = -0.2$, $\tau_i = 0.1$

$$\frac{dI}{dt} = (T - T_{sp}) \quad T_{sp} = 138.5^\circ\text{F}$$

9-14 (a)

Equations:

$d(C_a)/d(t) = ((F_{ao} - (C_a \cdot v_o))/V) + r_a$	<u>Initial value</u>
$d(C_b)/d(t) = (((3.45 - C_b) \cdot v_o)/V) + r_a$	0.0378
$d(C_c)/d(t) = (((D - C_c) \cdot v_o)/V) - r_a$	2.12
$d(C_m)/d(t) = (((C_{mo} - C_m) \cdot v_o)/V)$	0.0144
$d(T)/d(t) = ((m_c \cdot 18 \cdot (60 - (T - (0.41111 \cdot (T - 60)))) - ((F_{ao} \cdot 35) + 19950 \cdot (T - T_o)) + (36000 \cdot (-r_a \cdot V))) / ((35 \cdot C_a \cdot V) + (18 \cdot C_b \cdot V) + (46 \cdot C_a \cdot V) + (19.5 \cdot C_m \cdot V))$	0.2269
$d(I)/d(t) = T - T_{sp}$	133.5
$V = (1/7.484) \cdot 500$	0
$C_{mo} = 0.22696$	
$m_c = 1000$	
$T_o = 75$	
$T_{sp} = 138.5$	
$C_{ao} = 0.18157$	
$k = 16.96 \cdot 12 \cdot \exp(-32400 / (1.987 \cdot (T + 460)))$	
$C_{bo} = 2.2696$	
$kc = -0.2$	
$\tau_{ai} = 0.1$	
$F_{aoo} = 80$	
$r_a = -k \cdot C_a$	
$F_{ao} = F_{aoo} + ((kc / \tau_{ai}) \cdot I)$	
$v_o = (F_{ao} / 0.932) \cdot 354.8$	
$t_0 = 0, \quad t_f = 10$	

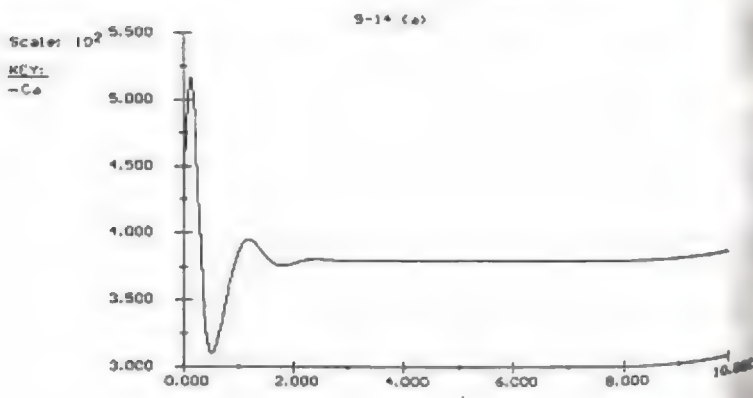
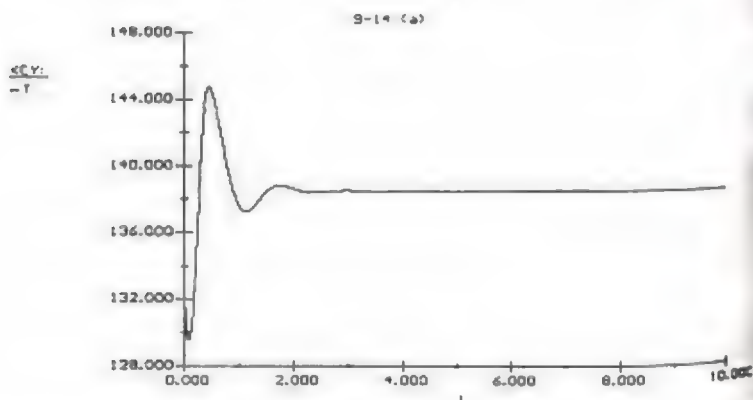
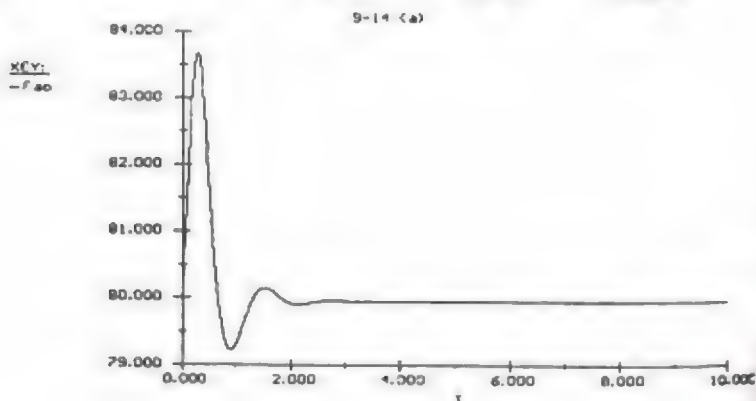
9-14 (a)

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	10	0	10
Ca	0.0378	0.051674	0.0309845	0.0379292
Cb	2.12	3.30833	2.12	3.30646
Cc	0.0144	0.151372	0.0144	0.143535
Cm	0.2269	0.22696	0.2269	0.22696
T	133.5	144.771	129.556	138.5
I	0	0.391858	-1.83983	0.0248276
V	66.8092	66.8092	66.8092	66.8092
Cmo	0.22696	0.22696	0.22696	0.22696
mc	1000	1000	1000	1000
To	75	75	75	75
Tsp	138.5	138.5	138.5	138.5
Cao	0.18157	0.18157	0.18157	0.18157
k	19.8379	33.1033	16.5058	24.9562
Cbo	2.2696	2.2696	2.2696	2.2696
kc	-0.2	-0.2	-0.2	-0.2

9-47

P9-14 cont'd

TAUI	0.1	0.1	0.1	0.1
Paoo	80	80	80	80
ra	-0.749871	-0.749871	-1.08581	-0.946566
Pao	80	83.6797	79.2163	79.9503
vo	440.637	444.585	439.796	440.584



9-48

P9-14 cont'd

Part (b)

I-control only :

manipulated variable = T_o

controlled variable = T

$$T_o = T_{oo} + \frac{kc}{u} I$$

where $T_{oo} = 75^\circ\text{F}$,

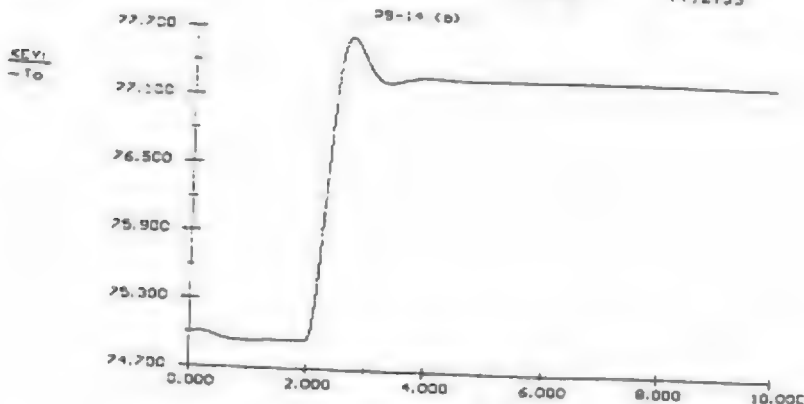
say $kc = -0.2$, $\tau_i = 0.1$

$$\frac{dT}{dt} = (T - T_{sp})$$

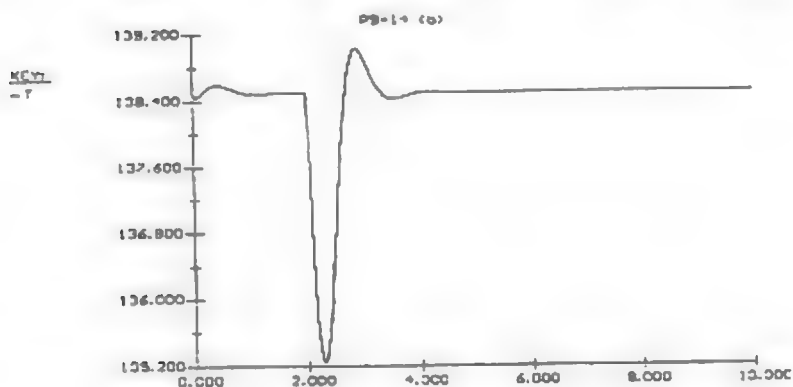
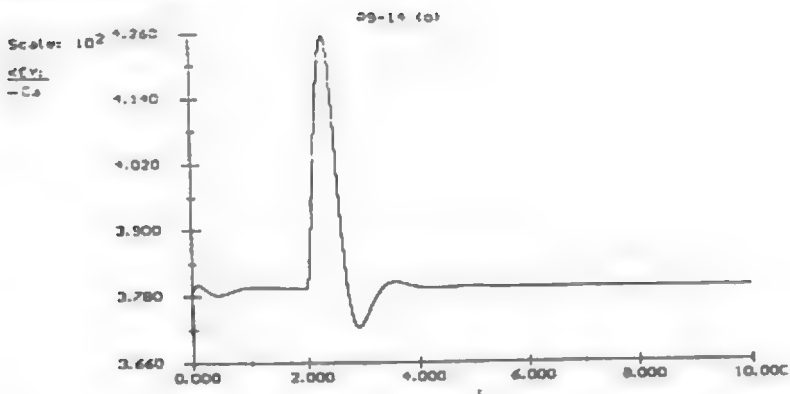
$T_{sp} = 138.5^\circ\text{F}$

P9-14 (b)

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	10	0	10
Ca	0.0378	0.0425433	0.0372412	0.0379524
Cb	3.3062	3.31097	3.30567	3.30638
Cc	0.0144	0.144329	0.0144	0.143618
Cm	0.2269	0.22696	0.2269	0.22696
T	138.5	139.035	135.24	138.5
I	0	0.032149	-1.31208	-1.13674
Cao	0.18157	0.18157	0.18157	0.18157
vo	440.6	440.6	440.6	440.6
v	66.8092	66.8092	66.8092	66.8092
Cmo	0.22696	0.22696	0.22696	0.22696
mc	1000	1000	1000	1000
Tal	60	60	55	55
Tsp	138.5	138.5	138.5	138.5
k	24.9561	25.5704	21.4966	24.9561
Cbo	2.2696	2.2696	2.2696	2.2696
Too	75	75	75	75
kc	-0.2	-0.2	-0.2	-0.2
tauI	0.1	0.1	0.1	0.1
ra	-0.943341	-0.907591	-0.955192	-0.947144
To	75	77.6242	74.9357	77.2735



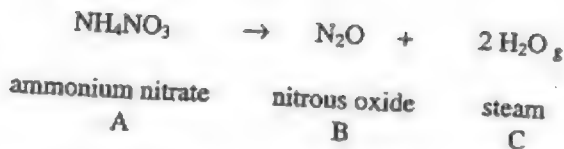
P9-14 cont'd



9-50

P9-15_a

CSTR



Feed, $m_o = m_{ao} + m_{co} = 0.83 \text{ mo} + 0.17 \text{ mo}$ ($m_{co} = 17\% \text{ liquid water in feed}$)

Mol balance : $\frac{dMa}{dt} = m_{ao} - 0 + r_a \cdot V$ $Ma = \text{lb A}, m_{ao} = \text{lb/h A}$

$$\frac{dMb}{dt} = 0 - mb - r_a \cdot V$$

leaving : $mb = m_{ao} \cdot \left(\theta_b + \frac{b}{a} X \right) = m_{ao}$; $\theta_b = 0, b/a = 1$
 ($X = 1$, i.e. all of A entering reacts, but there is some initially inside)

$$\frac{dMc}{dt} = m_{co} - mc - 2 \cdot r_a \cdot V$$

leaving : $mc = m_{ao} \cdot \left(\theta_c + \frac{c}{a} X \right) = m_{co} + 2m_{ao}$; $\theta_c \neq 0, c/a = 2$

steam. assuming all water entering with the ammonium nitrate leaves as

Rate law : $-r_a \cdot V = k \cdot C_a \cdot V = k \cdot Ma$

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E}{R \cdot T_2} - \frac{E}{R \cdot T_1}$$

$$\begin{aligned}
 E &= \frac{\ln\left(\frac{k_1}{k_2}\right)}{\frac{1}{R \cdot T_2} - \frac{1}{R \cdot T_1}} = \frac{\ln\left(\frac{0.53}{5.03}\right)}{\frac{1}{1.987(560+460)} - \frac{1}{1.987(510+460)}} \\
 &= 88500 \text{ Btu / lb mol}
 \end{aligned}$$

$$k = 0.53 \cdot \exp\left[\frac{88500}{1.987} \left(\frac{1}{510+460} - \frac{1}{T+460} \right)\right]$$

Energy balance :

P9-15 cont'd

$$\frac{dT}{dt} = \frac{Q - W_s - \sum m_{io}.C_{pi}(T - T_{io}) - m_{co}.(H_i - H_{io}) + (-\Delta H_{rx})(-r_a.V)}{\sum M_i.C_{pi}}$$

where

$$W_s = 0$$

$$Q = UA.(T_a - T)$$

$$\begin{aligned}\sum m_{io}.C_{pi}.(T - T_{io}) &= m_{ao}.C_{pa}.(T - T_{io}) \\ &= 0.83 \times 310 \times 0.38 \times (T - 200)\end{aligned}$$

$$\begin{aligned}m_{co}.(H_i - H_{io}) &= m_{co}.[H_g(T) - H_l(T_{io})] \\ &= 0.17 \times 310 \times [(1202 + 0.47(T - 500)) - 168]\end{aligned}$$

assumes all liquid water in feed leaves as steam.

$$\begin{aligned}H_g(T) &= H_g(T_{ref}) + C_{pg}.(T - T_{ref}) = 1202 + 0.47.(T - 500) \\ H_l(200) &= 168 \text{ Btu/lb}\end{aligned}$$

$$\sum M_i.C_{pi} = 0.38 M_a + C_{pb}.M_b + 0.47 M_c$$

From ChemCAD III physical properties systems:

$$\begin{aligned}C_{pb}(N_2O, 516^\circ F) &= 1065 \text{ J/kg.K} \cdot \left(\frac{1}{1055} \text{ Btu}\right) \cdot \left(0.454 \frac{1}{\text{kg}}\right) \cdot \left(\frac{516^\circ F}{542 K}\right) \\ &= 0.44 \text{ Btu/lb } N_2O. K\end{aligned}$$

Part (a)

$$\text{at } t = 0 \quad C_a = 500 \text{ lb}, \quad T = 516^\circ F$$

$$\frac{dT}{dt} = \frac{10000.(515 - T) - 97.77(T - 200) - 52.7[(1202 + 0.47(T - 500)) - 168] + 336.(-r_a.V)}{0.38 M_a + 0.44.M_b + 0.47 M_c}$$

P9-15 cont'd

P9-15 (a)

Equations:

$$d(Ma)/dt = (310 - 0.83) \cdot raV$$

$$d(Mb)/dt = -mb - raV$$

$$d(Mc)/dt = mco - mc - (2 \cdot raV)$$

$$d(T)/dt = ((10000 \cdot (515 - T)) - (99.77 \cdot (T - 200)) - (52.7 \cdot (1202 + (0.47 \cdot (T - 500))) - 268) \cdot (336 \cdot (-raV))) / ((0.38 \cdot Ma) + (0.44 \cdot Mb) + (0.47 \cdot Mc))$$

$$mco = 310 \cdot 0.17$$

$$mao = 310 \cdot 0.83$$

$$k = 0.53 \cdot \exp(44540 \cdot ((1/970) - (1/(T + 460))))$$

$$raV = -k \cdot Ma$$

$$mb = mao$$

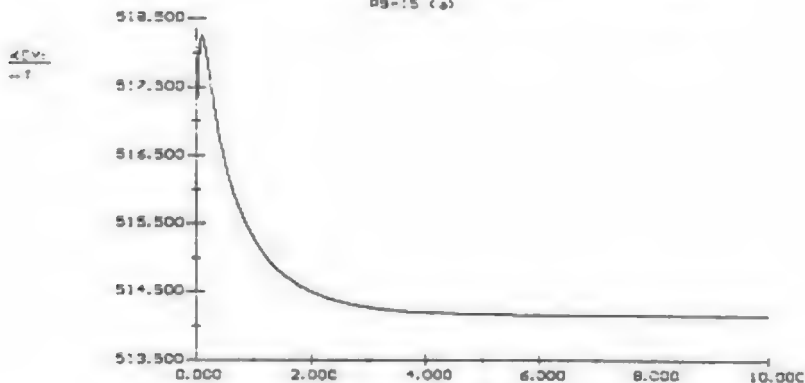
$$mc = mco + (2 \cdot mao)$$

$$t_0 = 0, \quad t_f = 10$$

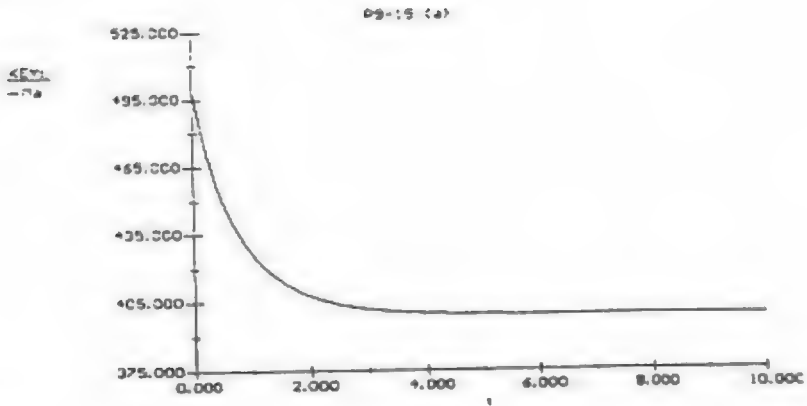
P9-15 (a)

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	10	0	10
Ma	500	500	399.067	399.067
Mb	0	100.933	0	100.933
Mc	0	201.866	0	201.866
T	516	518.255	514.158	514.158
mco	52.7	52.7	52.7	52.7
mao	257.3	257.3	257.3	257.3
k	0.702859	0.78083	0.644758	0.644758
raV	-351.43	-257.301	-382.097	-257.301
mb	257.3	257.3	257.3	257.3
mc	567.3	567.3	567.3	567.3

P9-15 (a)



P9-15 cont'd



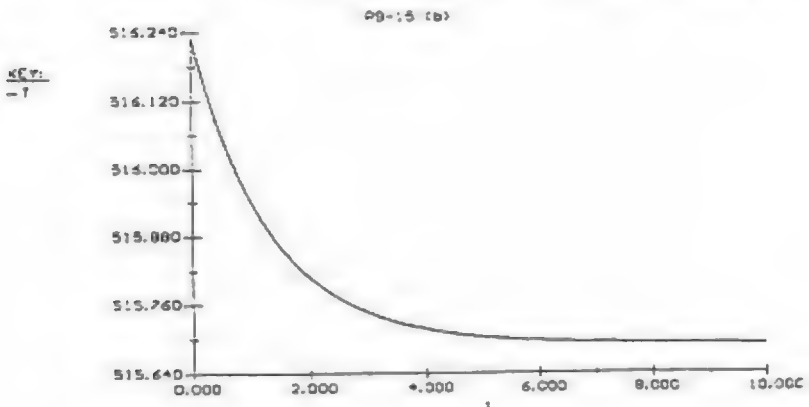
Part (b)

$$UA = 10000 \text{ Btu/h.ft}^2$$

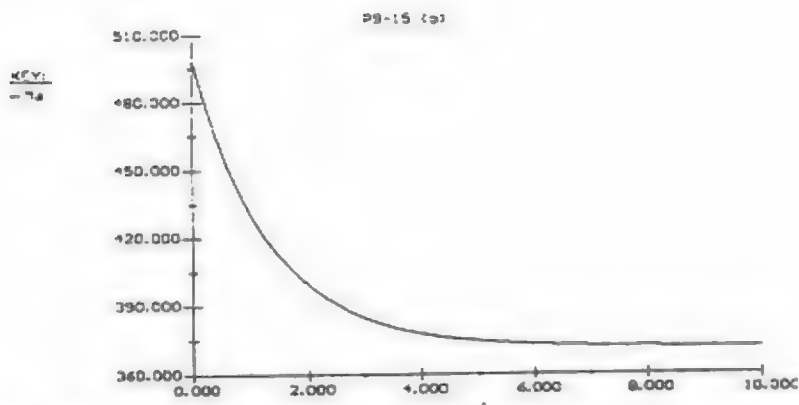
P-control only : manipulated variable = T_a
 controlled variable = T

$$T_a = T_{ao} + k_c(T - T_{sp})$$

where $T_{sp} = 516^\circ\text{F}$, $k_c = -5$, $T_{ao} = 975^\circ\text{R} = 515^\circ\text{F}$



P9-15 cont'd



Part (c)

$$UA = 10000 \text{ Btu/h.ft}^2$$

PI-control :

manipulated variable = T_a

controlled variable = T

$$T_a = T_{ao} + k_c \cdot (T - T_{sp}) + \frac{k_c}{v} \cdot I$$

$$\frac{dI}{dt} = (T - T_{sp})$$

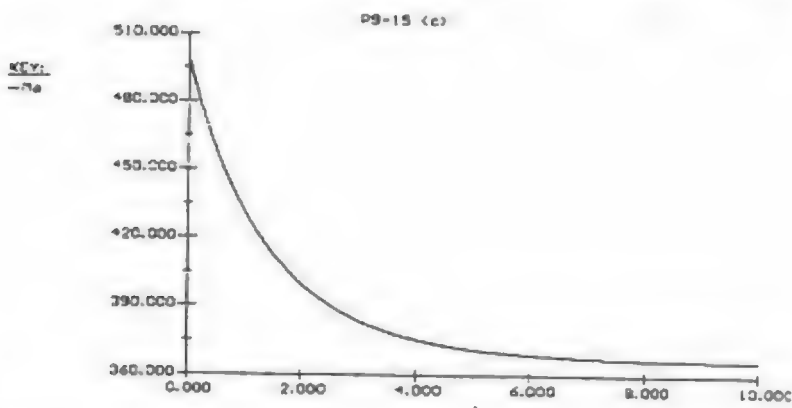
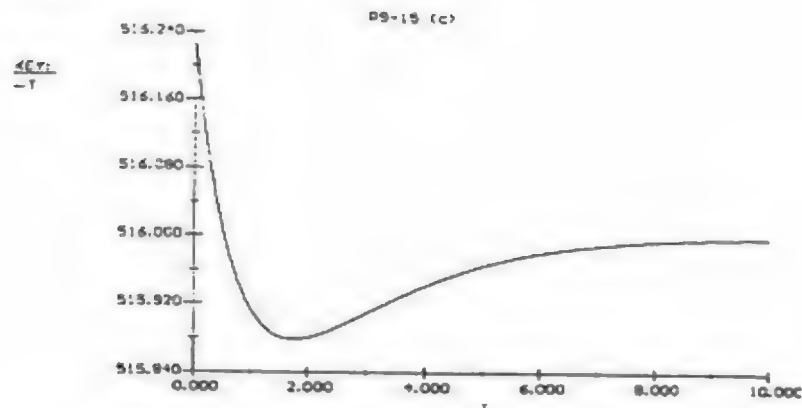
where $T_{sp} = 516^\circ\text{F}$, $k_c = -5$, $\tau_i = 1$, $T_{ao} = 975^\circ\text{R} = 515^\circ\text{F}$

P9-15 (c)

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	10	0	10
M_a	500	500	366.32	366.32
M_b	0	133.68	0	133.68
M_c	0	267.359	0	267.359
T	516	516.228	515.878	515.998
I	0	0.055709	-0.369513	-0.369513
M	500	767.359	500	767.359
T_{sp}	516	516	516	516
k	0.702859	0.710394	0.698867	0.702792
T_{ao}	515	515	515	515
m_{ao}	310	310	310	310
m_{ao}	257.3	257.3	257.3	257.3
k_c	-5	-5	-5	-5
τ_{ai}	1	1	1	1
r_{av}	-351.43	-257.447	-354.393	-257.447
m_b	257.3	257.3	257.3	257.3

9-55

P9-15 cont'd



Part (d)

$$UA = 10000 \text{ Btu/h.ft}^2$$

PI-control loop 1 : manipulated variable = T_a
controlled variable = T

$$T_a = T_{ao} + k_{cl} \cdot (T - T_{sp}) + \frac{k_{cl}}{\tau_I} \cdot I_1$$

$$\frac{dI_1}{dt} = (T - T_{sp})$$

where $T_{sp} = 516^\circ\text{F}$, $k_{cl} = -5$, $\tau_I = 1$, $T_{ao} = 975^\circ\text{R} = 515^\circ\text{F}$

PI-control loop 2 : manipulated variable = m_{ao}
controlled variable = $M (= M_a + M_b + M_c)$

P9-15 cont'd

$$m_{ao} = m_{aoo} + kc_2 \cdot (M - M_{sp}) + \frac{kc_2}{u_2} \cdot I_2$$

$$\frac{dI_2}{dt} = (M - M_{sp})$$

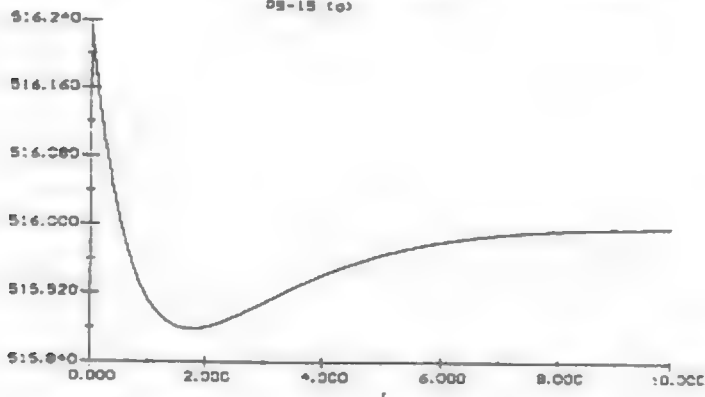
where $M_{sp} = 500$ lb, $kc_2 = 25$, $\tau_{I2} = 1$, $m_{aoo} = 310$ lb/h

P9-15 (d)

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	10	0	10
M _a	500	500	366.32	366.32
M _b	0	44.5579	0	44.5579
M _c	0	89.1157	0	89.1157
T	516	516.228	515.878	515.998
I ₂	0	0.055698	-2.09812	-2.09812
I ₁	0	0.0556442	-0.369506	-0.369506
M	500	500.416	499.317	499.994
M _{sp}	500	500	500	500
T _{sp}	516	516	516	516
k	0.702859	0.710395	0.69887	0.702792
T _{ao}	515	515	515	515
m _{aoo}	310	310	310	310
kc ₂	25	25	25	25
kc ₁	-5	-5	-5	-5
tau _{I1}	1	1	1	1
tau _{I2}	1	1	1	1
raV	-351.43	-257.447	-354.394	-257.447
T _a	515	516.858	513.843	516.858
m _{ao}	310	320.708	257.397	257.397
m _b	310	320.708	257.397	257.397
m _{co}	63.494	65.6872	52.7198	52.7198
m _c	683.494	707.104	567.513	567.513

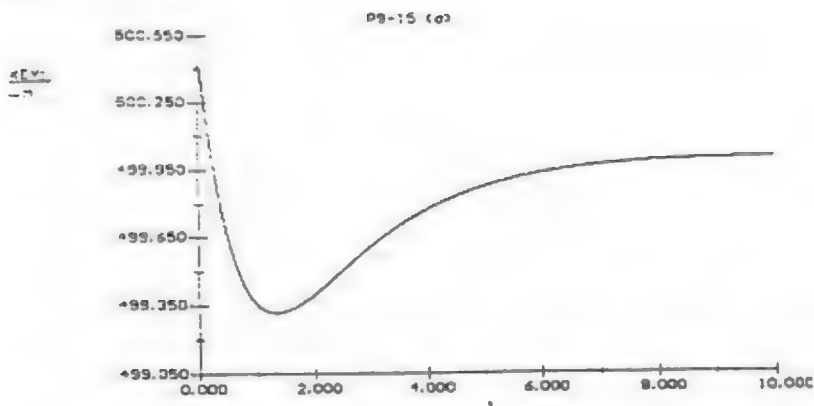
P9-15 (e)

KEY:
-T



9-57

P9-15 cont'd



P9-16

a) Plot $R(T)$ vs $G(T)$:

$$R(T) = UA(T - T_s) + \rho v_0 C_p (T - T_0)$$

$$G(T) = -\Delta H_{Rx} V k C_A$$

Evaluate the parameters in those equations:

$$k = 2 * 7.08 * 10^{11} \exp(-30000 / 1.987 / T)$$

$$\Delta H_{Rx} = -30000 \text{ BTU / lbmol}$$

$$\rho = 50 \text{ lb / ft}^3$$

$$UA = 150 * 250 = 37500$$

Use the following POLYMATH program to achieve the correct graph.

P9-16 cont'd

Equations:

$$d(T)/d(t)=1$$

$$dhr_{rxn}=-30000$$

$$V=48$$

$$C_{A0}=0.5$$

$$v_0=400$$

$$UA=250 \times 150$$

$$T_a=530$$

$$\rho=50$$

$$C_p=.75$$

$$T_0=530$$

$$E=30000$$

$$k=2 \times 7.08 \times 10^{11} \exp(-E/1.987/T)$$

$$\tau=v_0/v_0$$

$$C_A=C_{A0}/(1+\tau k)$$

$$Q_r=UA \cdot (T-T_a) + \rho v_0 C_p (T-T_0)$$

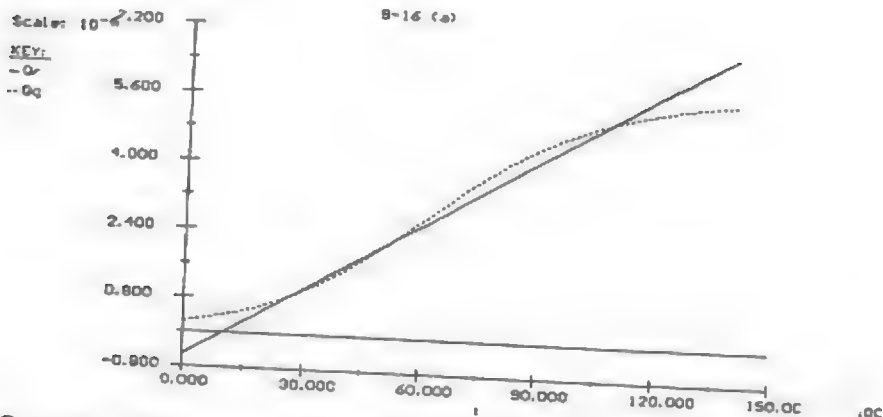
$$Q_g=-dhr_{rxn} \cdot V \cdot k \cdot C_A$$

$$\Delta T=Q_r-Q_g$$

$$t_0 = 0, \quad t_f = 140$$

Initial value

530



b) On the graph we can see that there are three steady states. We can use the following POLYMATH program to find the exact numbers of the steady-state with the design equation for a CSTR and the temperatures at which $G(T)$ and $R(T)$ intersect.

$$V = \frac{v_0(C_{A0} - C_A)}{kC_A}$$

$$R(T) - G(T) = 0$$

P9-16 cont'd

Equations:

$$f(C_A) = v_0 \cdot (C_{A0} - C_A) / V - k \cdot C_A$$

$$f(T) = Q_R - Q_G$$

$$v_0 = 400$$

$$C_{A0} = .5$$

$$V = 48$$

$$E = 30000$$

$$UA = 150 \cdot 250$$

$$T_a = 530$$

$$\rho \cdot v_0 = 50$$

$$T_0 = 530$$

$$C_p = .75$$

$$dH_{rxn} = -30000$$

$$k = 2 \cdot 7.08 \cdot 10^{11} \cdot \exp(-E/1.987/T)$$

$$Q_G = -dH_{rxn} \cdot V \cdot k \cdot C_A$$

$$Q_R = UA \cdot (T - T_a) + \rho \cdot v_0 \cdot (T - T_0) \cdot C_p$$

9-16 b

Variable	Solution Value	f()
C _A	0.406429	-2.22e-16
T	542.245	-2.31e-09
v ₀	400	
C _{A0}	0.5	
V	48	
E	30000	
UA	37500	
T _a	530	
ρ · v ₀	50	
T ₀	530	
C _p	0.75	
dH _{rxn}	-30000	
k	1	
Q _G	642857	
Q _R	642857	

Variable	Solution Value	f()
C _A	0.31974	-7.117e-15
T	571.263	-8.382e-09
v ₀	400	
C _{A0}	0.5	
V	48	
E	30000	
UA	37500	
T _a	530	
ρ · v ₀	50	
T ₀	530	
C _p	0.75	
dH _{rxn}	-30000	
k	4.72885	
Q _G	2.16632e+06	
Q _R	2.16632e+06	

Variable	Solution Value	f()
C _A	0.068429	-5.292e-15
T	628.645	-6.519e-09
v ₀	400	
C _{A0}	0.5	
V	48	
E	30000	
UA	37500	
T _a	530	
ρ · v ₀	50	
T ₀	530	
C _p	0.75	
dH _{rxn}	-30000	
k	52.5567	
Q _G	5.17885e+06	
Q _R	5.17885e+06	

The exact values are: C_A = 0.425 T = 547.1°R

C_A = 0.319 T = 571.3°R

C_A = 0.068 T = 628.6°R

The extinction temperature is around 555°R

c) Using the unsteady-state equations for a CSTR we get the following Mole balance:

$$\frac{dC_A}{dt} = \frac{v_0(C_{A0} - C_A)}{V} - kC_A$$

Energy balance:

$$\frac{dT}{dt} = \frac{UA(T_a - T) - \rho v_0 C_p (T - T_0) - \Delta H_{rxn} k C_A V}{\rho V C_p}$$

From these we can plug into POLYMATH and come up with the following graphs.

9-60

P9-16 cont'd

Equations:

$$d(ca)/d(t) = vo * (cao - ca) / V - k * ca$$

$$d(T)/d(t) = (UA * (Ta - T) - rho * vo * Cp * (T - To) - dhrxm * k * ca * V) / (rho * V * Cp)$$

$$d(T1)/d(t) = (J * tau * k * ca - (1 + kappa) * (T - Tc)) / tau$$

$$vo = 400$$

$$cao = .5$$

$$V = 48$$

$$UA = 250 * 150$$

$$Ta = 530$$

$$rho = 50$$

$$Cp = .75$$

$$To = 530$$

$$dhrxm = -30000$$

$$E = 30000$$

$$R = 1.987$$

$$k = 2 * 7.08 * 10^{11} * \exp(-E/R/T)$$

$$tau = V/vo$$

$$J = -dhrxm / rho / Cp$$

$$kappa = UA / rho / vo / Cp$$

$$Tc = (Ta - kappa + To) / (1 + kappa)$$

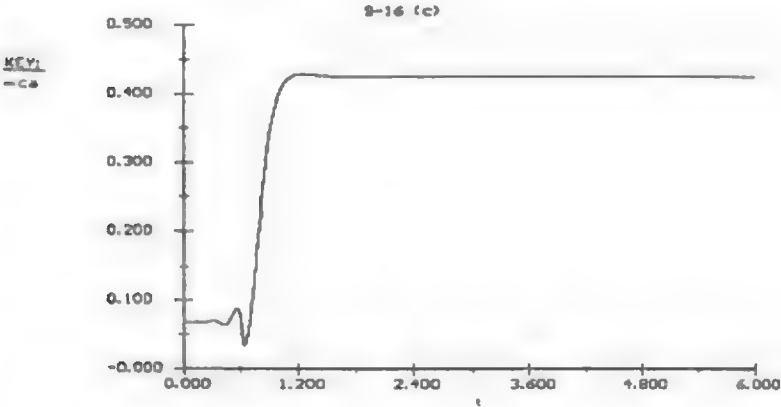
$$t_0 = 0, \quad t_f = 6$$

Initial value

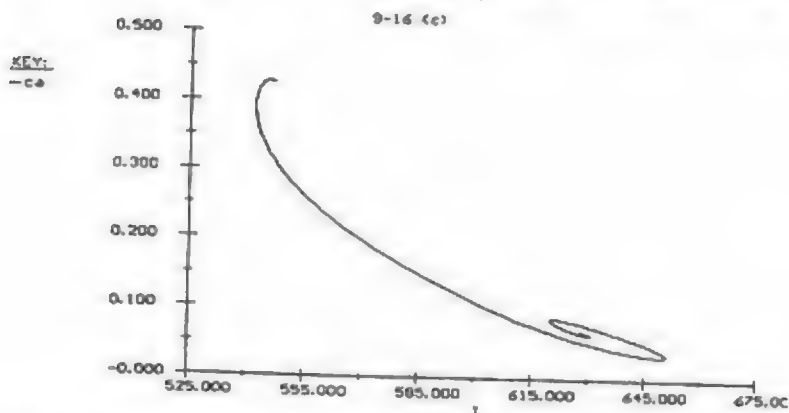
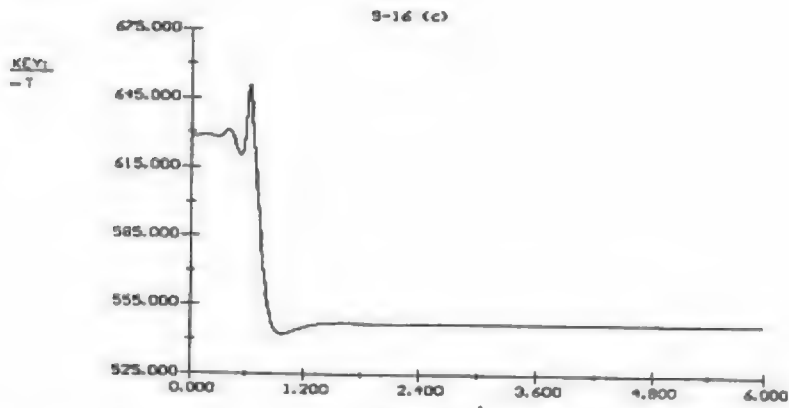
$$0.0684$$

$$628.645$$

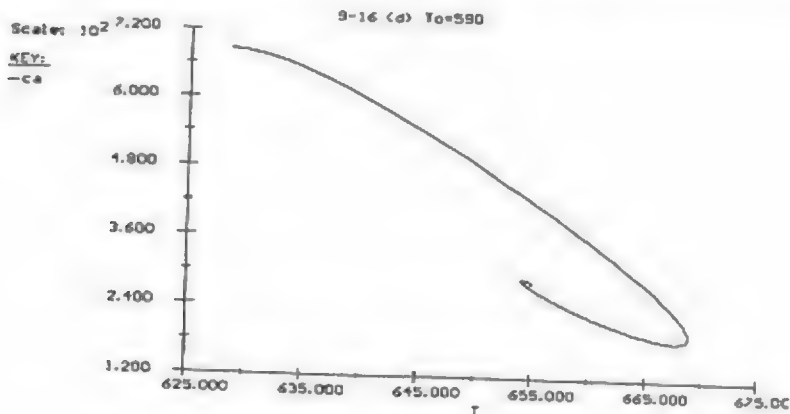
$$628.645$$



P9-16 cont'd

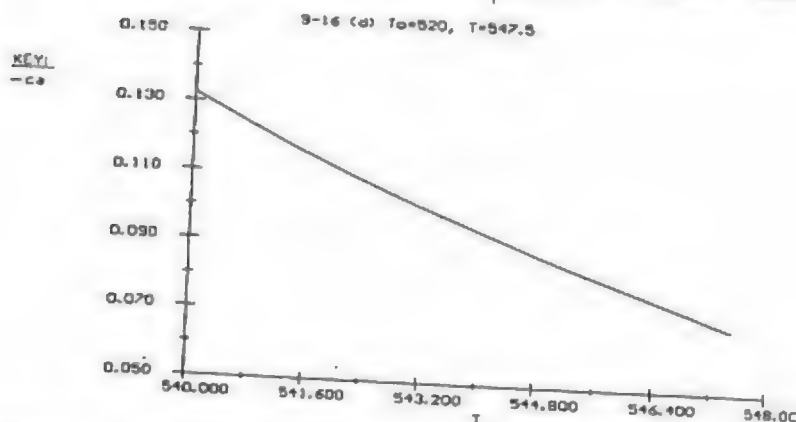
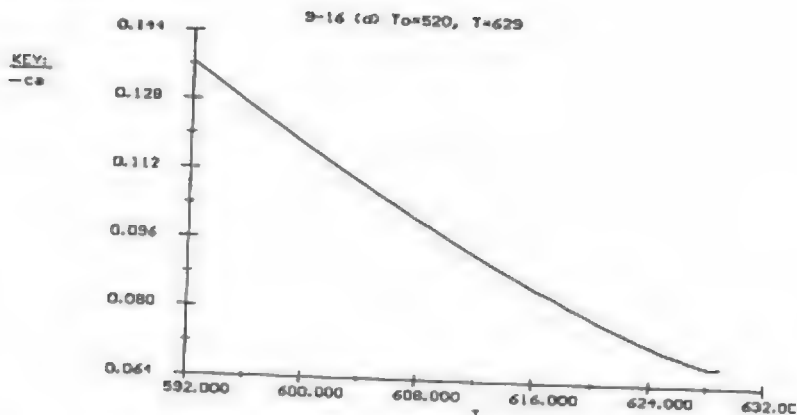


d) By varying to $T = 547.5^{\circ}\text{R}$ we get the following graphs which show a stable steady-state.



9-62

P2-16 cont'd



Varying $T_0 = 590$ shows that it is an unstable steady-state.

$T_0 = 520$, $T = 629$ it stabilizes towards the lower steady-state.

$T_0 = 520$, $T = 547.5$ is stable.

e) The graphs for C_A and T have already been created so we just need equations for x_1 and y_1 .

$$\frac{dx}{dt} = \frac{-L \cdot x + \frac{N}{J} y}{\tau}$$

$$\frac{dy}{dt} = \frac{J(1-L)x - (M-N)y}{\tau}$$

where

$$L = 7.1$$

$$N = 14.21$$

9-63

P9-16 cont'd

$$J = \frac{-\Delta H_{Rx}}{\rho C_p}$$

$$M = 3.5$$

$$\tau = \frac{V}{v_0}$$

then

$$x1 = \frac{x}{0.0684}$$

$$y1 = \frac{y}{628}$$

Plugging this into POLYMATH gives the following graphs.

9-16 (e)

Equations:

$$d(ca)/d(t) = v_0 * (cao - ca) / V - k * ca$$

$$d(T)/d(t) = (UA * (Ta - T) - \rho ho * v_0 * Cp * (T - To) - dhrxm * k * ca * V) / (\rho ho * V * Cp)$$

$$d(x)/d(t) = (-L * x + N / J * y) / \tau$$

$$d(y)/d(t) = (J * (1 - L) * x - (N * N) * y) / \tau$$

$$v_0 = 400$$

$$cao = .5$$

$$V = 48$$

$$UA = 150 * 250$$

$$Ta = 530$$

$$\rho ho = 50$$

$$Cp = .75$$

$$To = 530$$

$$dhrxm = -30000$$

$$L = 7.1$$

$$N = 14.21$$

$$M = 3.5$$

$$N = 30000$$

$$y1 = y / 628$$

$$x1 = x / .0684$$

$$k = 2 * 7.08 * 10^{11} * \exp(-E / 1.987 / T)$$

$$\tau = V / v_0$$

$$J = -dhrxm / \rho ho / Cp$$

$$t_0 = 0, \quad t_f = 6$$

Initial value

$$0.0684$$

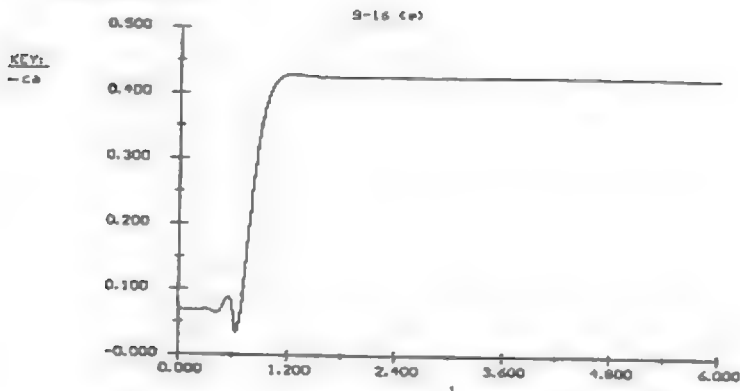
$$628.645$$

$$-0.02$$

$$-2$$

9-64

P9-16 cont'd



f) No solution will be given.

g) The following POLYMATH program gives the linear analysis of the problem.

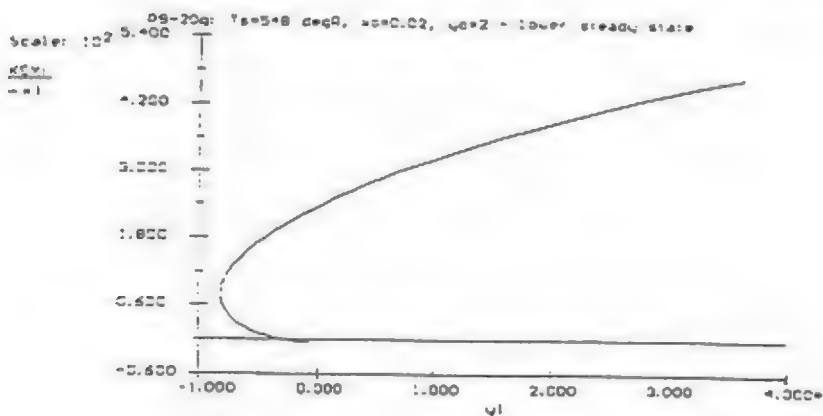
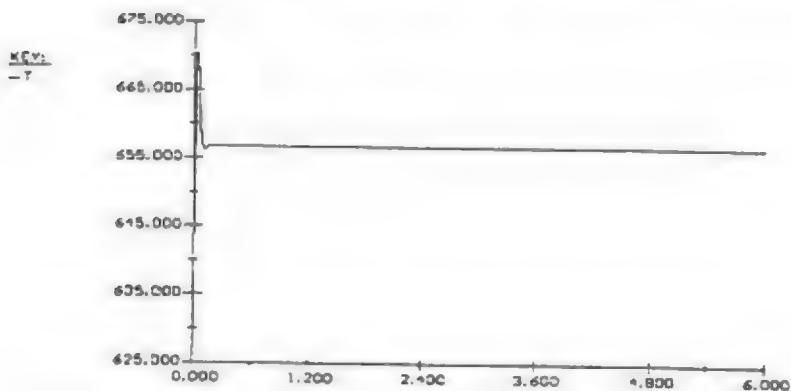
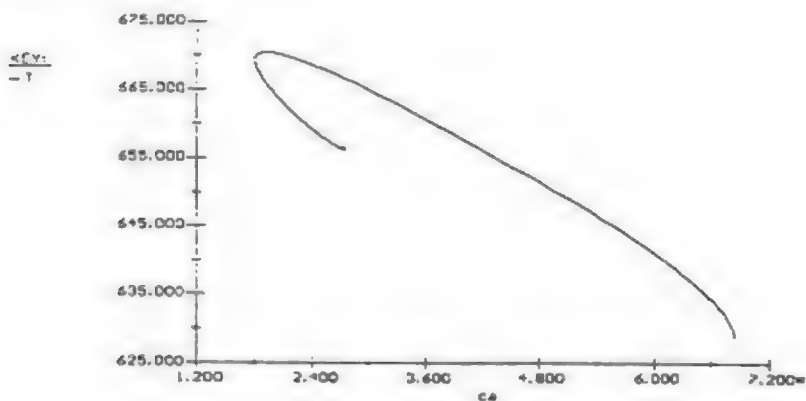
$L = 1.021$, $M = 2.51$, $N = 2.51$, $\tau = .12$, $J = 800$

```

9-16 (g)
Equations:
d(ca)/d(t)=vo*(cao-ca)/V-k*ca          Initial value 0.0684
d(T)/d(t)=(UA*(Ta-T)-rho*vo*Cp*(T-To)-dhrm*k*ca*V)/(rho*  628.645
V*Cp)
d(x)/d(t)=(-L*x+N/J*y)/tau             0.02
d(y)/d(t)=(J*(1-L)*x-(M*N)*y)/tau      2
vo=400
cao=.5
V=48
UA=150*250
Ta=530
rho=50
Cp=.75
To=595
dhrm=-30000
L=1.021
N=2.51
M=2.51
B=30000
A=2*7.08*10^11
Cas=0.04253
Ts=547
k=2*7.08*10^11*exp(-E/1.987/T)
y1=y/Ts
x1=x/Cas
tau=V/vo
J=-dhrm/rho/Cp
c=L*M-N
b=L+N-N
kappa=UA/rho/vo/Cp
Tc=(Ta*kappa-To)/(1+kappa)
Qg=J*tau*k*ca/tau
Qr=(1+kappa)*(T-Tc)/tau
t0 = 0,    tf = 6
    
```

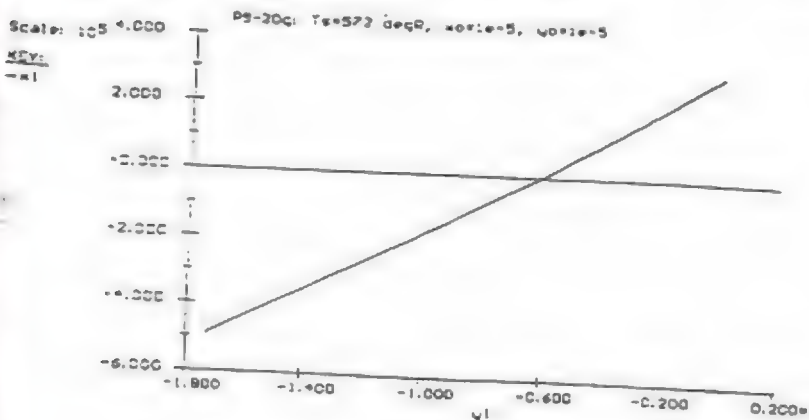
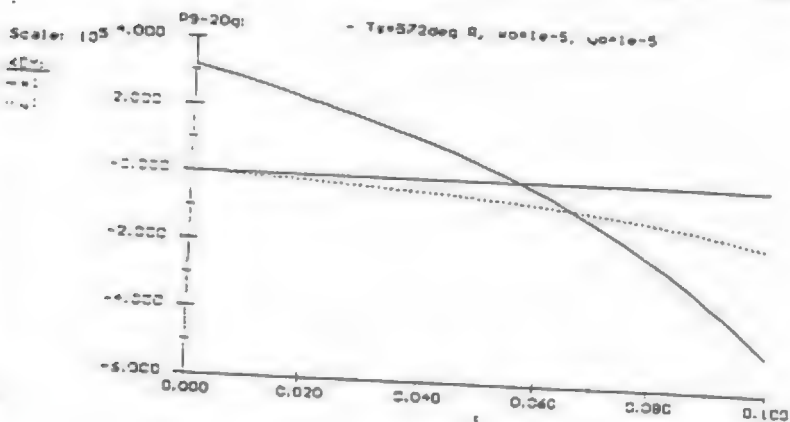
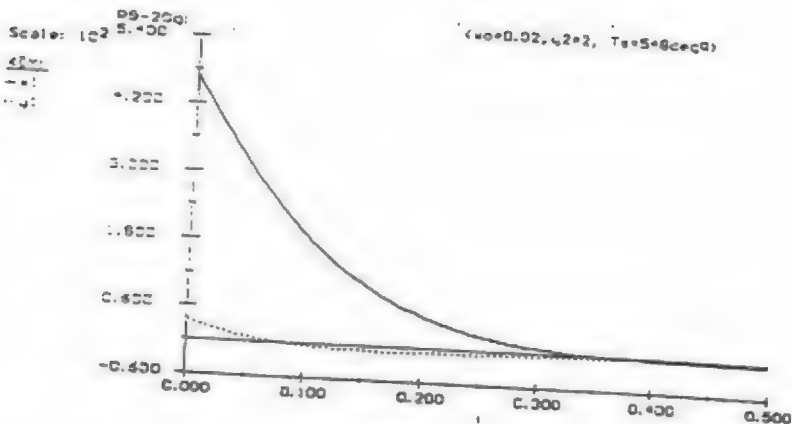
9-65

P9-16 cont'd



9-66

P9-16 cont'd



P9-17_a

Batch reactor - series reaction

Mol balance on A : $\frac{dC_a}{dt} = r_{a1}$

$$-r_{a1} = k_1.C_a \quad C_a = C_{a0}.\exp(-k_1.t)$$

Mol balance on B : $\frac{dC_b}{dt} = r_{b1} + r_{b2}$

$$r_{b1} = -r_{a1} = k_1.C_a \quad \text{and} \quad -r_{b2} = k_2.C_b$$

$$\frac{dC_b}{dt} = k_1.C_{a0}.\exp(-k_1.t) - k_2.C_b$$

Mol balance on C : $\frac{dC_c}{dt} = -r_{b2}$

$$k_1 = 3.03.\exp\left(\frac{9900}{1.987}\left(\frac{1}{300} - \frac{1}{T}\right)\right)$$

$$k_2 = 4.58.\exp\left(\frac{27000}{1.987}\left(\frac{1}{500} - \frac{1}{T}\right)\right)$$

Energy balance : $\frac{dT}{dt} = \frac{Q + (-\Delta H_{rx1})(-r_{a1}.V) + (-\Delta H_{rx2})(-r_{b2}.V)}{\sum N_i.C_{pi}}$

$$Q = UA.(T_a - T)$$

$$\sum N_i.C_{pi} = C_a.V.C_{pa} + C_b.V.C_{pb} + C_c.V.C_{pc}$$

$$\frac{dT}{dt} = \frac{UA.(330 - T) + 55000(-r_{a1}.V) + 71500(-r_{b2}.V)}{200.V.(C_a + C_b + C_c)}$$

P9-17 cont'd

Part (a)

$$UA = 0$$

$$\frac{dT}{dt} = \frac{V[55000(-ra1.) + 71500(-rb2.)]}{200.V.(Ca + Cb + Cc)}$$

P9-17 (a)

Equations:

$$d(Ca)/d(t) = ra1$$

$$d(Cc)/d(t) = -rb2$$

$$d(Cb)/d(t) = rb1 + rb2$$

$$d(T)/d(t) = ((UA \cdot (330 - T)) + (55000 \cdot (-ra1 \cdot V)) + (71500 \cdot (-rb2 \cdot V))) / (200 \cdot V \cdot (Ca + Cb + Cc))$$

$$UA = 0$$

$$V = 10$$

$$k1 = 3.03 \cdot \exp((9900/1.987) \cdot ((1/300) - (1/T)))$$

$$k2 = 4.58 \cdot \exp((27000/1.987) \cdot ((1/500) - (1/T)))$$

$$ra1 = -k1 \cdot Ca$$

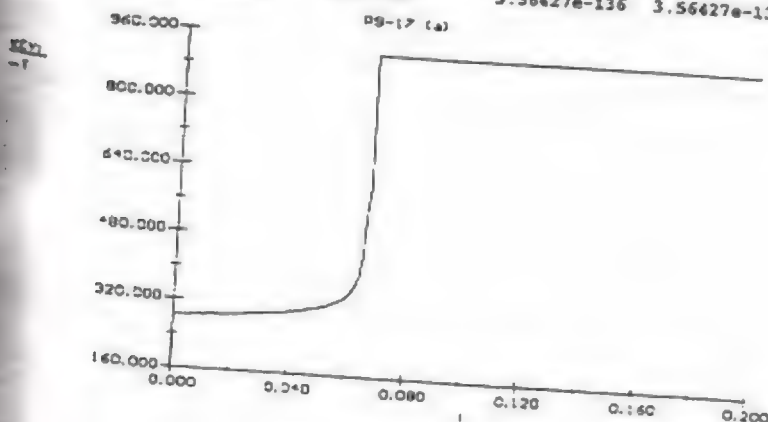
$$rb2 = -k2 \cdot Cb$$

$$rb1 = -ra1$$

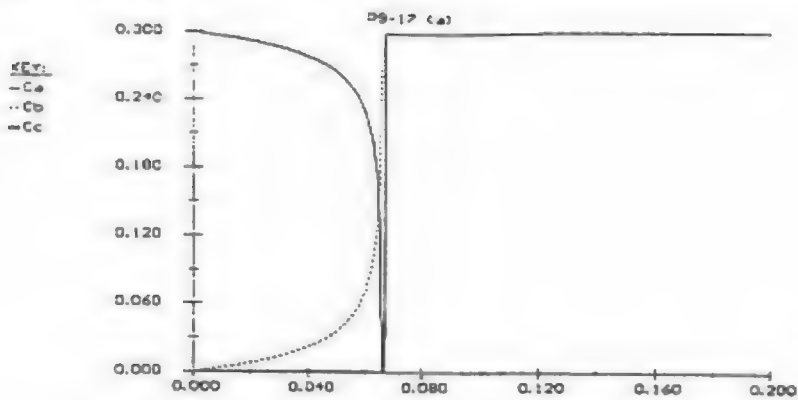
$$t_0 = 0, \quad t_f = 0.2$$

P9-17 (a)

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	0.2	0	0.2
Ca	0.3	0.3	0	0.2
Cc	0	0.3	1.66467e-141	1.66467e-141
Cb	0	0.286701	0	0.3
T	283	915.5	0	4.30972e-142
UA	0	0	283	915.5
V	10	10	0	0
k1	1.1173	214113	10	10
k2	4.08097e-09	1.04114e+06	1.1173	214113
ra1	-0.335189	-3.56427e-136	4.08097e-09	1.04114e+06
rb2	-0	-0	-144.724	-3.56427e-136
rb1	0.335189	144.724	-18607.3	-4.48704e-136
			3.56427e-136	3.56427e-136



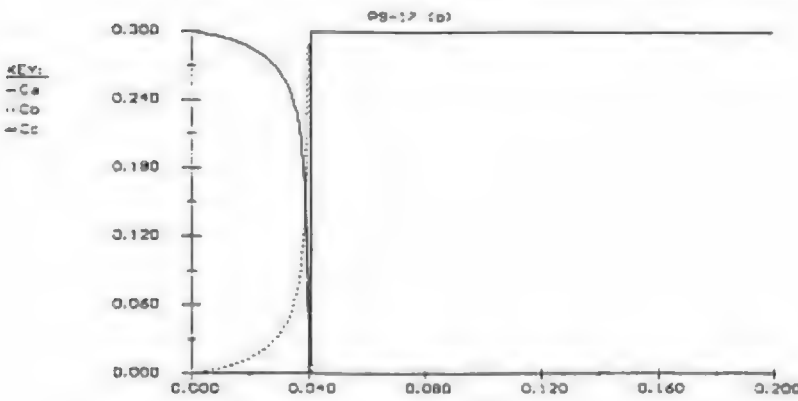
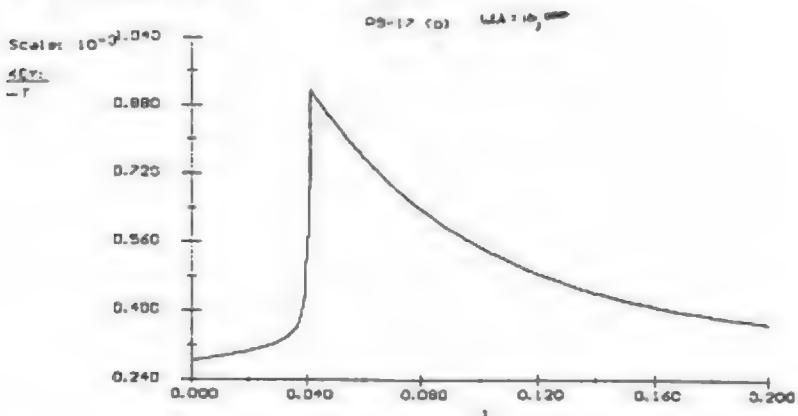
P9-17 cont'd



Part (b)

$UA = 10000 \text{ J/min.K}$

$V = 10 \text{ dm}^3$

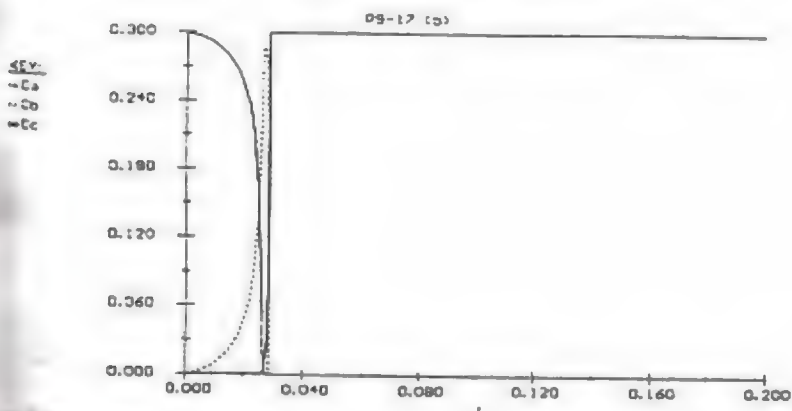
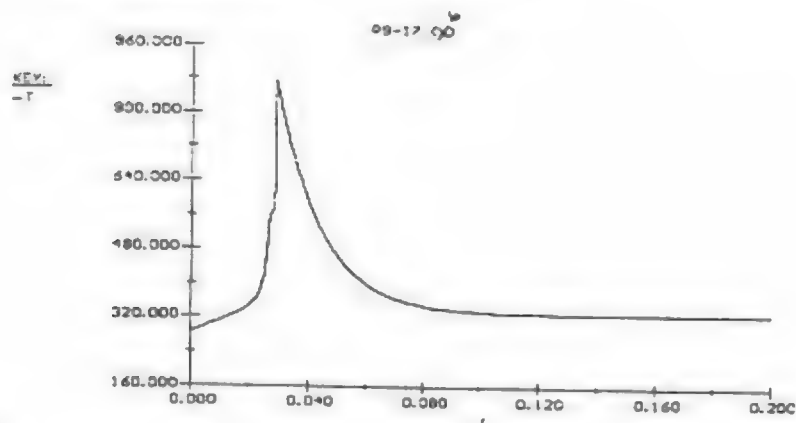


P9-17 cont'd

Part (b)

$$UA = 40000 \text{ J/min.K}$$

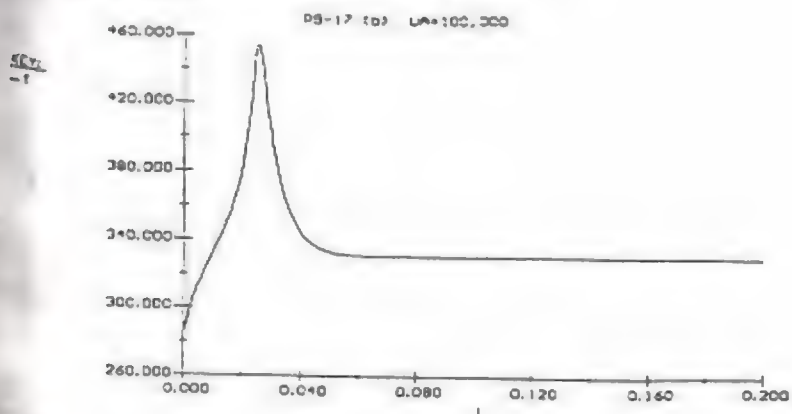
$$V = 10 \text{ dm}^3$$



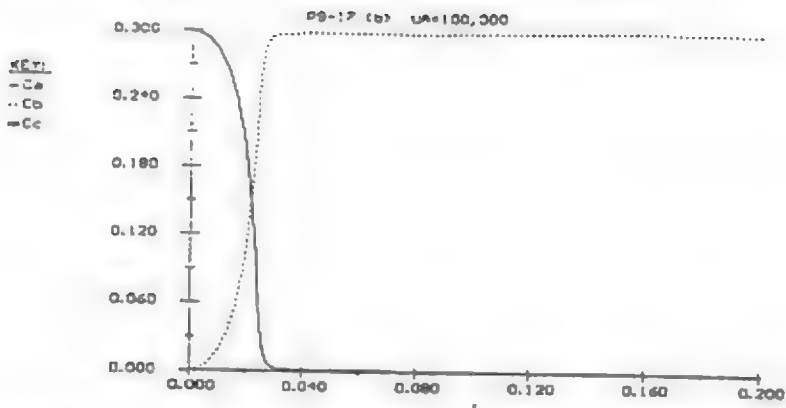
Part (b)

$$UA = 100000 \text{ J/min.K}$$

$$V = 10 \text{ dm}^3$$



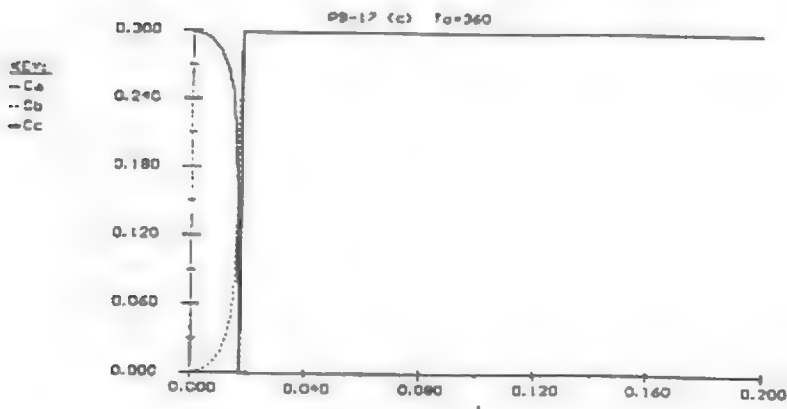
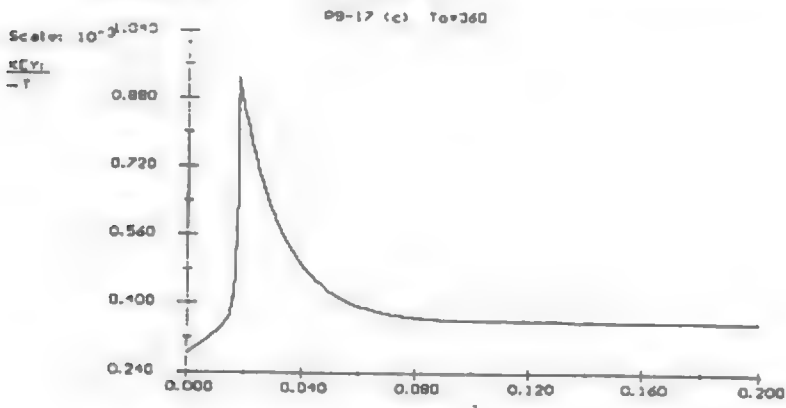
P9-17 cont'd



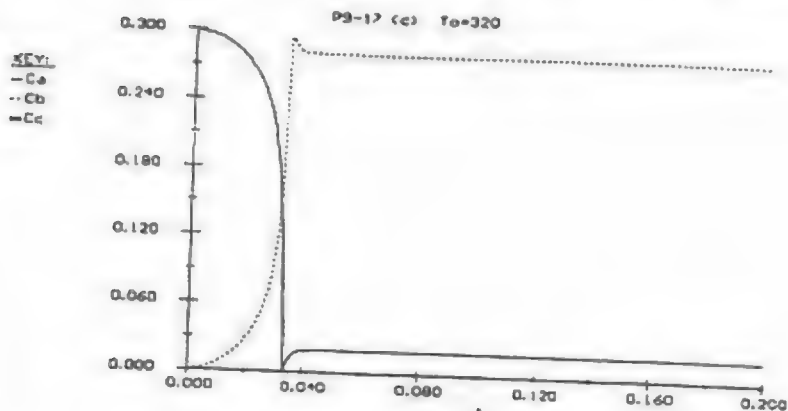
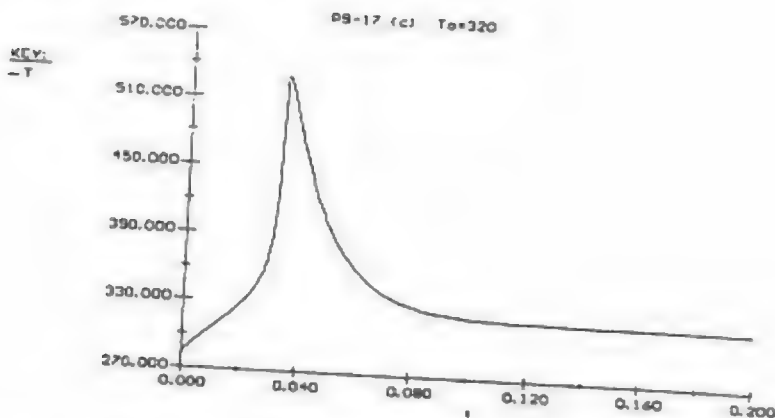
At $UA = 10,000 \text{ J/min.K}$ the 2nd reaction for C is totally suppressed
 Part (c)

$UA = 40,000 \text{ J/min.K}$

$T_0 = 320 \text{ K}$



P9-17 cont'd



P9-18_B

Semibatch with parallel reactions

Mol balance :

$$\frac{dN_a}{dt} = F_{a0} + (r_1 + r_2) \cdot V \quad \frac{dN_b}{dt} = F_{b0} + (r_1 + r_2) \cdot V$$

$$\frac{dN_d}{dt} = -r_1 \cdot V \quad \frac{dN_u}{dt} = -r_2 \cdot V$$

Rate laws :

$$-r_1 = k_1 \cdot C_a$$

$$-r_2 = k_2 \cdot C_b$$

$$k_1 = 1000 \cdot \exp\left(-\frac{2000}{T}\right)$$

$$k_2 = 2000 \cdot \exp\left(-\frac{3000}{T}\right)$$

P9-18 cont'd

Stoichiometry :

$$C_a = \frac{N_a}{V}$$

$$C_b = \frac{N_b}{V}$$

$$C_d = \frac{N_d}{V}$$

$$C_u = \frac{N_u}{V}$$

$$V = V_0 + v_a.t + v_b.t$$

$$\text{assume } V_0 = 0$$

$$v_a = \frac{F_{a0}}{C_{a0}}$$

$$v_b = \frac{F_{b0}}{C_{b0}}$$

$$C_{a0} = 5 \text{ mol/dm}^3$$

$$C_{b0} = 4 \text{ mol/dm}^3$$

$$V = v_0.t$$

$$\text{where } v_0 = \frac{F_{a0}}{C_{a0}} + \frac{F_{b0}}{C_{b0}}$$

$$\text{But } F_{a0} = F_{b0} \text{ (equimolar feed)}$$

$$v_0 = 0.45.F_{a0}$$

$$V = 0.45 F_{a0}.t$$

Energy balance :

$$\frac{dT}{dt} = \frac{Q - W_s - \sum F_{i0}.C_{pi}.(T - T_{i0}) + (-\Delta H_{rx}(T)).(-r_a.V)}{\sum N_i.C_{pi}}$$

$$\text{where } Q = W_s = 0$$

$$\Delta H_{rx}(T) = \Delta H_{rx}(T_{ref}) + \Delta C_p(T - T_{ref})$$

$$\Delta C_{p1} = \frac{d}{a}.C_{pd} - \frac{b}{a}.C_{pb} - C_{pa} = 50 - 20 - 30 = 0$$

$$\Delta H_{rx1}(T) = -3000 \text{ cal/mol A}$$

$$\Delta C_{p2} = \frac{u}{a}.C_{pu} - \frac{b}{a}.C_{pb} - C_{pa} = 40 - 20 - 30 = -10$$

$$\Delta H_{rx2}(T) = -5000 - 10.(T - 300)$$

$$\sum F_{i0}.C_{pi}.(T - T_{i0}) = 20.F_{a0}.(T - T_{a0}) + 30.F_{b0}.(T - T_{b0})$$

$$\sum N_i.C_{pi} = N_a.C_{pa} + N_b.C_{pb} + N_d.C_{pd} + N_u.C_{pu}$$

9-7 4

P9-18 cont'd

$$\frac{dT}{dt} = \frac{20.F_{Ao}(T - T_{Ao}) + 30.F_{Bo}(T - T_{Bo}) + 3000.(-r_1.V) + [5000 + 10(T - 300)](-r_2.V)}{20.N_a + 30.N_b + 50.N_d + 40.N_u}$$

$$\text{Selectivity } S = \frac{r_1}{r_2}$$

Part (a)

The selectivity is insensitive to v_0 and T_0 (as the reactor is initially empty) but it is sensitive to T_{i0} . The ratio of k_1 to k_2 dictates S , and from the given relationships between k_1 and k_2 with T , it is seen that a lower operating temperature is preferable for increased selectivity for D over U. Therefore ambient temperature feed is used (although cooling may increase the 1st reaction, extra costs would be incurred.)

Choose $T_i = 298 \text{ K}$ $T_{Ao} = 298 \text{ K}$ $T_{Bo} = 298 \text{ K}$ $v_0 = 20 \text{ mol/min}$

P9-18 (a)

Equations:

$$d(N_a)/d(t) = ((r_1 + r_2) \cdot V) + F_{Ao}$$

$$d(N_b)/d(t) = ((r_1 + r_2) \cdot V) - F_{Bo}$$

$$d(N_d)/d(t) = -r_1 \cdot V$$

$$d(N_u)/d(t) = -r_2 \cdot V$$

$$d(T)/d(t) = ((-20 \cdot F_{Ao} \cdot (T - T_{Ao})) - (30 \cdot F_{Bo} \cdot (T - T_{Bo})) + (3000 \cdot (-r_1 \cdot V)) + ((5000 + (10 \cdot (T - 300))) \cdot (-r_2 \cdot V))) / ((20 \cdot N_a) + (50 \cdot N_d) + (40 \cdot N_u))$$

Initial value

0.001

0.001

0

0

298

$$T_{Ao} = 298$$

$$T_{Bo} = 298$$

$$k_1 = 1000 \cdot \exp(-2000/T)$$

$$k_2 = 2000 \cdot \exp(-3000/T)$$

$$v_0 = 20$$

$$F_{Ao} = v_0 / 0.45$$

$$V = 0.45 \cdot F_{Ao} \cdot t$$

$$F_{Bo} = F_{Ao}$$

$$C_a = N_a / V$$

$$C_b = N_b / V$$

$$C_d = N_d / V$$

$$C_u = N_u / V$$

$$r_1 = -k_1 \cdot C_b$$

$$r_2 = -k_2 \cdot C_b$$

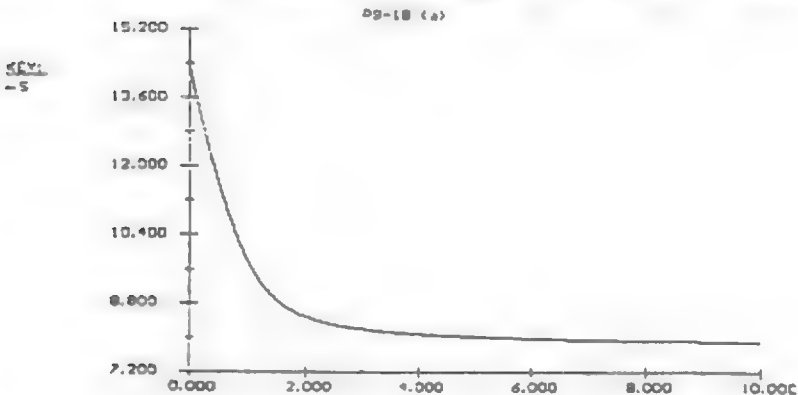
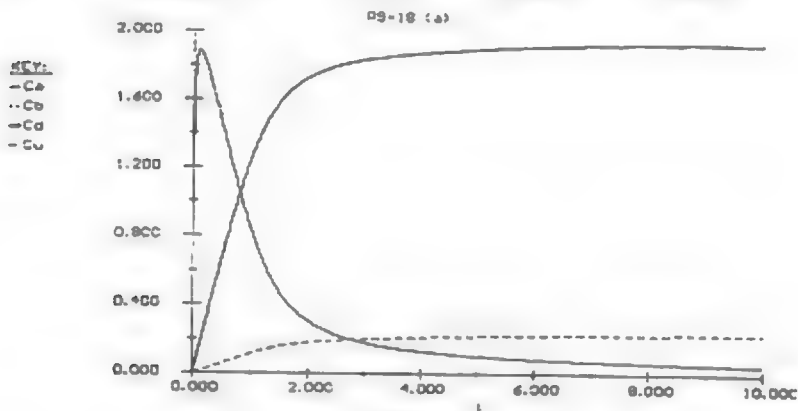
$$S = r_1 / r_2$$

$$t_0 = 0.01, \quad t_f = 10$$

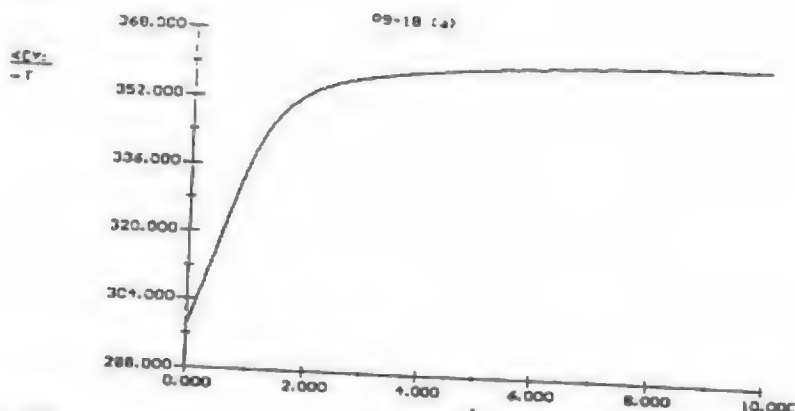
P9-18 cont'd

P9-18 (a)

Variable	Initial value	Maximum value	Minimum value	Final value
t	0.01	10	0.01	10
Na	0.001	17.0418	0.001	9.86331
Nb	0.001	17.0418	0.001	9.86331
Nd	0	387.317	0	387.317
Nu	0	46.8212	0	46.8212
T	298	362.267	298	362.267
Tao	298	298	298	298
Tbo	298	298	298	298
k1	1.21695	4.00271	1.21695	4.00271
k2	0.0849059	0.506478	0.0849059	0.506478
vo	20	20	20	20
Fao	44.4444	44.4444	44.4444	44.4444
V	0.2	200	0.2	200
Fbo	44.4444	44.4444	44.4444	44.4444
Ca	0.005	1.88957	0.005	0.0493165
Cb	0.005	1.88957	0.005	0.0493165
Cd	0	1.93658	0	1.93658
Cu	0	0.234106	0	0.234106
r1	-0.00608474	-0.00608474	-2.70229	-0.1974
r2	-0.00042453	-0.00042453	-0.235535	-0.0249777
S	14.3329	14.3329	7.90302	7.90302



P9-18 cont'd



Part (b)

Let the rate laws be :

$$-r_1 = k_1.C_b$$

$$-r_2 = k_2.C_a$$

⇒ No change in the system. (S ~ 7.8)

Let the rate laws be :

$$-r_1 = k_1.C_a.C_b$$

$$-r_2 = k_2.C_a.C_b$$

$$-r_1 = k_1.C_a$$

$$-r_2 = k_2.C_a$$

$$-r_1 = k_1.C_b$$

$$-r_2 = k_2.C_b$$

⇒ Small selectivity increase. (S ~ 8)

Let the rate laws be :

$$-r_1 = k_1.C_a.C_b$$

$$-r_2 = k_2.C_a$$

$$-r_1 = k_1.C_a.C_b$$

$$-r_2 = k_2.C_b$$

⇒ Large selectivity decrease. (S ~ 1.3)

Let the rate laws be :

$$-r_1 = k_1.C_a$$

$$-r_2 = k_2.C_a.C_b$$

$$-r_1 = k_1.C_b$$

$$-r_2 = k_2.C_a.C_b$$

⇒ Huge selectivity increase. (S ~ 138)

The decreasing concentrations of A and B (below 1.0) with time act to suppress the reaction rates to varying degrees depending on the order. A 2nd order reaction is suppressed much more than a 1st order reaction, hence the large selectivity in the latter two instances where the second reaction is second order.

P9-18 cont'd

Part (c)

ΔH_{rx1} cal/mol A	$\Delta H_{rx2}(300K)$ cal/mol A	Temp. K	Selectivity S
3000	5000	362	7.9
5000	5000	399	6.1
10000	5000	484	3.9
1000	5000	323	11.0
3000	1000	354	8.5
3000	10000	375	7.2

If ΔH_{rx2} is constant, then if ΔH_{rx1} increases, T increases and S decreases.

If ΔH_{rx1} is constant, then if $\Delta H_{rx2}(300K)$ increases, T increases and S decreases.

S is dependent on r_1 and r_2 , which depend on k_1 and k_2 , which depend on the temperature. The greater the temperature in the reactor the smaller the ratio between k_1 and k_2 , hence reduced S.

Chapter 10

- P10-1.** An open-ended problem that requires students to create and original problem and solution.
- P10-2.** "What if. . ." problem. A number of parts to this problem require descriptive answers. Part (h) involves a parameter sensitivity of **Living Example Problem 10-7**.

P10-3. This problem is quite straight forward and is often used as an introduction problem on catalysis.

Problems **P10-4**, **P10-5**, **P10-6**, **P10-8**, **P10-9**, and **P10-10** all give data and ask the student to find the rate law, mechanism, and rate limiting step for a catalytic reaction. I would choose one problem from **P10-4** through **P10-6** and one problem from **P10-8** through **P10-10**. First choices might be **P10-6** and **P10-8** which are the most straight forward.

P10-7. This problem is similar to **P10-3**, but is more complicated.

P10-11. This problem is better adapted for a senior or graduate level course.

Problems **P10-12** through **P10-14** all concern chemical vapor deposition where the student is asked to find the rate law, mechanism and rate limiting step. In the past **P10-13** has been assigned as a homework problem and **P10-14** as a problem worked in class.

P10-15. California problem.

P10-16. This problem uses **Living Example Problem E10-5** to apply to a moving bed reactor and to a PBR modeled as CSTRs in series. It is fairly advanced and may be best suited for a senior or graduate level course.

Problems **P10-17** through **P10-27** all involve catalyst decay.

P10-18. A very straight forward, but with a trap for those who go to quickly.

P10-19. is fairly straight forward using POLYMATH. If time is an issue, one can omit part (e).

P10-20. Uses real data from which the student is asked to determine the decay law parameters.

P10-21. This problem builds on **Living Example Problem 10-7** and asks to recommend operating conditions.

P10-22. Part (a) is typically assigned from year to year. The remaining problems (P10-17 through P10-27) are more complicated and are more appropriate for a second undergraduate course or a graduate course.

P10-27. This problem encompasses the effects of catalyst decay with heat effects and is a typical digital age problem

Summary

	<u>Assigned</u>	<u>Alternates</u>	<u>Difficulty</u>	<u>Time</u>	<u>Solution Given</u>
P10-1					
P10-2					
P10-3					
P10-4					
P10-5					
P10-6					
P10-7					
P10-8					
P10-9					
P10-10					
P10-11					
P10-12					
P10-13					
P10-14					
P10-15					
P10-16					
P10-17					
P10-18					
P10-19					
P10-20					
P10-21					
P10-22					
P10-23					
P10-24					
P10-25					
P10-26					
P10-27					
CDP10-A					
CDP10-B					
CDP10-C					
CDP10-D					
CDP10-E					
CDP10-F					
CDP10-G					

CDP10-H

CDP10-I

CD10-J

Assigned

- = Always assigned, AA = Always assign one from the group of alternates, O = Often, I = Infrequently, S = Seldom, G = Graduate level

Alternates

In problems that have a dot in conjunction with AA means that one of the problems, either the problem with a dot or any one of the alternates are always assigned.

Time

Approximate time in minutes it would take a B/B* student to solve the problem.

Difficulty

SF = Straight forward reinforcement of principles (plug and chug)

FSF = Fairly straight forward (requires some manipulation of equations or an intermediate calculation).

IC = Intermediate calculation required

M = More difficult

OE = Some parts open-ended.

Note the letter problems are found on the CD-ROM. For example A = CDP1-A.

Summary Table Ch-10

Cataly

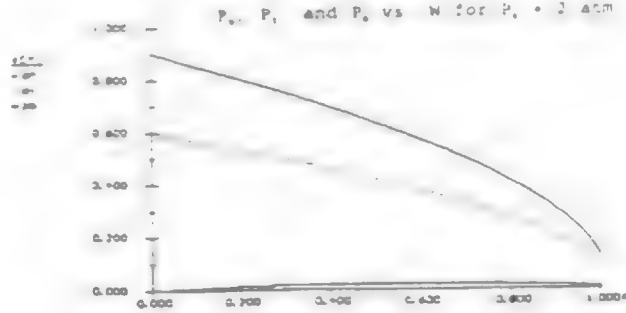
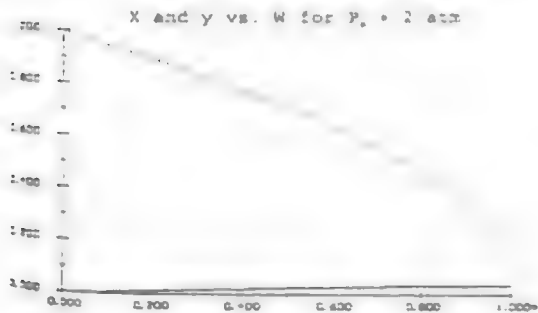
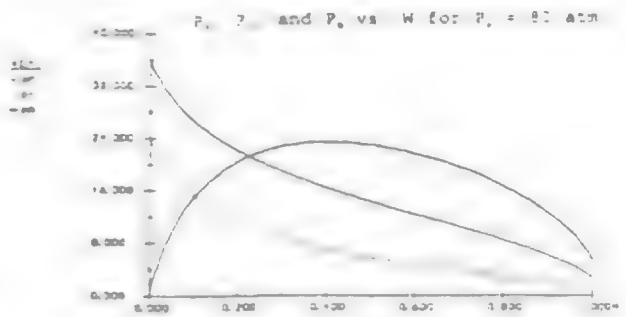
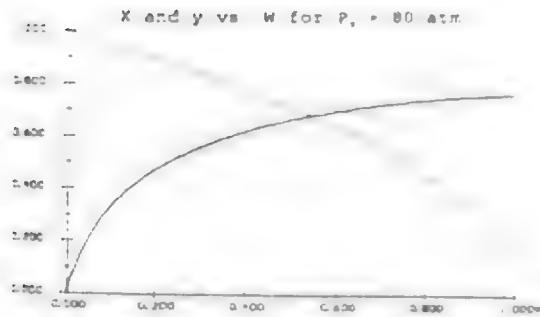
	Catalysis	CVD	Order	T vs. t Traj	Moving Bed	STTR
Basic Reinforcement Principles	3					
Straight forward	4,5,9,18	13,14			18	
Fairly Straight Forward	6,7,9,10, 15	12	17,12(a)	16(d)	16(a),14(b), 22(b),2_(b)	24(d)
More Difficult	7(c),11		23,24,25, 26	20,21(e)	16(c),27	
Open-ended				16(e)		
Critical Thinking					24(d)	

Chapter 10

P10-1 No solution will be given.

P10-2

- (a) Use the equations from Example 10-3 in POLYMATH. Change P_0 to 80 atm and then to 2 atm. The effects can be seen in the following four graphs:



- (b) Temperature-time trajectories for 1st and 2nd order decay.

Case 1

$$E_A = 35 \text{ kcal/mol} \quad E_d = 10 \text{ kcal/mol} \quad d_{00} = 0.01 \text{ day}^{-1} \quad T_0 = 400 \text{ K}$$

1st order decay:

$$t = \frac{E_A}{k_{d0} E_d} \left[1 - \exp \left[\frac{E_d}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \right] = \frac{35}{(0.01)(10)} \left[1 - \exp \left[\frac{10}{0.001987} \left(\frac{1}{T} - \frac{1}{400} \right) \right] \right]$$

$$t = 350 \left[1 - \exp \left[5033 \left(\frac{1}{T} - \frac{1}{400} \right) \right] \right]$$

10-5

P10-2 (cont'd)

2nd order decay:

$$t = \frac{1 - \exp\left[\frac{E_d - E_A}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]}{k_{\infty} (E_d/E_A - 1)} = -140 \left[1 - \exp\left[-12,582 \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \right]$$

Case 2

$$E_A = 10 \text{ kcal/mol}$$

$$E_d = 35 \text{ kcal/mol}$$

$$d_{\infty} = 0.01 \text{ day}^{-1}$$

$$T_0 = 400 \text{ K}$$

1st order decay:

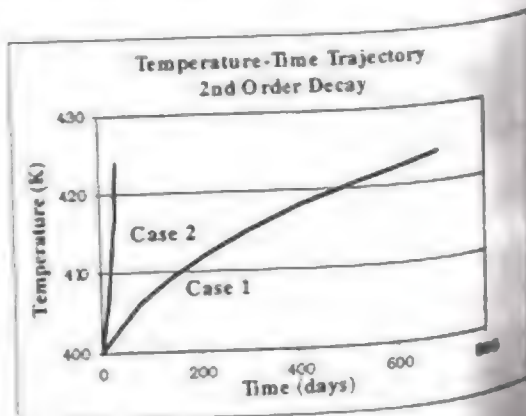
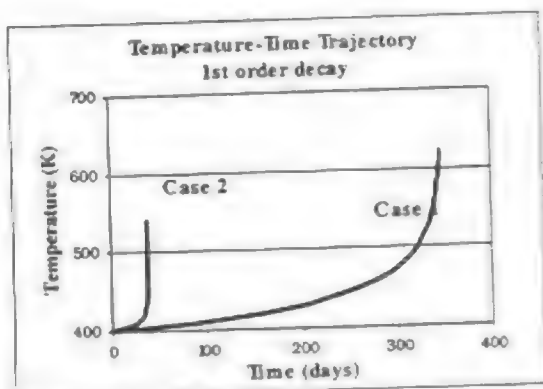
$$t = \frac{E_A}{k_{\infty} E_d} \left[1 - \exp\left[\frac{E_d}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \right] = \frac{10}{(0.01)(35)} \left[1 - \exp\left[\frac{35}{0.001987} \left(\frac{1}{T} - \frac{1}{400}\right)\right] \right]$$

$$t = 38.57 \left[1 - \exp\left[17,614 \left(\frac{1}{T} - \frac{1}{400}\right)\right] \right]$$

2nd order decay:

$$t = \frac{1 - \exp\left[\frac{E_d - E_A}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]}{k_{\infty} (E_d/E_A - 1)} = 40 \left[1 - \exp\left[12,582 \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \right]$$

Use these equations in Excel to generate the following graphs:



- (c) Use the POLYMATH program from Example 10-5.

By simply changing the value of τ we can see its effect on the minimum concentration. An increase in τ causes a decrease in the minimum concentration, while a decrease in τ causes an increase in concentration.

When the reactor is full of inerts, the catalyst lifetime is longer

When we change the values of k and k_d to 120 and 12 respectively, we see a decrease in the catalyst lifetime.

- (d) Again use the POLYMATH program from Example 10-5. When τ is changed to 0.005 h, $C_{A_{min}} = 0.607 \text{ mol/dm}^3$. When τ is changed to 0.01 h, $C_{A_{min}} = 0.509 \text{ mol/dm}^3$.
- (e) For the solids and reactants entering from different ends of the reactor:

Decay Law: (for 1st order decay) $\frac{da}{dt} = -k_d a$

$$dt = \frac{dW}{U_s} \Rightarrow \frac{da}{dW} = \frac{k_d}{U_s} a \Rightarrow \frac{da}{a} = \frac{k_d}{U_s} dW$$

$$\ln(a) = \frac{k_d}{U_s} W + k_1$$

$$\text{For } W = W_{max}, a = 1: \quad \ln(1) = 0 = \frac{k_d}{U_s} W_{max} + k_1$$

$$k_1 = -\frac{k_d}{U_s} W_{max} \Rightarrow \ln(a) = \frac{k_d}{U_s} (W - W_{max})$$

$$a = \exp\left[\frac{k_d}{U_s} (W - W_{max})\right]$$

Combine: $F_{A_0} \frac{dX}{dW} = \exp\left[\frac{k_d}{U_s} (W - W_{max})\right] k C_{A_0}^2 (1-X)^2$

$$\int_0^X \frac{dX}{(1-X)^2} = \frac{k C_{A_0}^2}{F_{A_0}} \int_0^W \exp\left[\frac{k_d}{U_s} (W - W_{max})\right] dW$$

$$\frac{X}{1-X} = \frac{k C_{A_0}^2 U_s}{F_{A_0} k_d} \left[1 - \exp\left(\frac{k_d}{U_s} (-W_{max})\right) \right]$$

$$\frac{X}{1-X} = \frac{(0.6)(0.075)^2 (10,000)}{(30)(0.72)} \left[1 - \exp\left(\frac{0.72}{10,000} (-22,000)\right) \right] = 1.2419$$

$$X = 0.55$$

(f)

Design Equation: $F_{A0} \frac{dX}{dW} = a(W)(-r_A)$

Rate Law: $-r_A = kC_A^2$

Decay Law: $-\frac{da}{dt} = k_d a^2 \Rightarrow -\frac{da}{dt} = \frac{k_d}{U_s} a^2 \Rightarrow a = \frac{1}{1 + \left(\frac{k_d}{U_s}\right)W}$
 $W = 0, a = 1$

Stoichiometry: $C_A = C_{A0}(1-X)$

Combining: $F_{A0} \frac{dX}{dW} = \frac{1}{1 + \left(\frac{k_d}{U_s}\right)W} kC_{A0}^2(1-X)^2$

$$\frac{F_{A0}}{kC_{A0}^2} \int_0^X \frac{dX}{(1-X)^2} = \int_0^W \frac{dW}{1 + \frac{k_d}{U_s} W} \Rightarrow \frac{F_{A0}}{kC_{A0}^2} \left(\frac{X}{1-X} \right) = \frac{U_s}{k_d} \ln \left(1 + \frac{k_d}{U_s} W \right)$$

$$\frac{(30)(1.24)}{(0.6)(0.075)^2} = y(\ln(1 + 22000/y)) \quad \text{where } y = \frac{U_s}{k_d}$$

$$y = 8796.12 \text{ gcat} = \frac{U_s}{k_d} \Rightarrow U_s = 6333.2 \text{ gcat/min}$$

(g)

$$C_A = C_{A0} \frac{1-X}{1+\varepsilon X} = C_{A0} \frac{1-X}{1+2X}$$

Combining:

$$F_{A0} \frac{dX}{dW} = e^{-(k_d/U_s)W} kC_{A0}^2 \left(\frac{1-X}{1+2X} \right)^2$$

$$\int_0^X \left(\frac{1-X}{1+2X} \right)^2 dX = \frac{kC_{A0}^2}{F_{A0}} \int_0^W e^{-(k_d/U_s)W} dW$$

$$4(1+2) \ln(1-X) + 4X + \frac{9X}{1-X} = \frac{kC_{A0}^2 U_s}{F_{A0} k_d} (1 - e^{-X, W/U_s})$$

$$12 \ln(1-X) + 4X + \frac{9X}{1-X} = 1.24$$

$$\text{Solve for } X \Rightarrow X = 0.37$$

37% Conversion

10-8

P10-2 (cont'd)

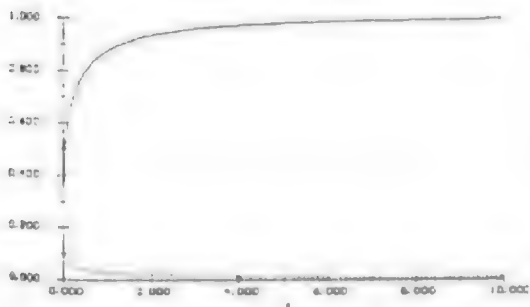
- (h) Use the POLYMATH program given in the example problem and vary all of the stated parameters.

k' has the largest effect on the conversion, followed by A , U_e , and P_{Ag} .

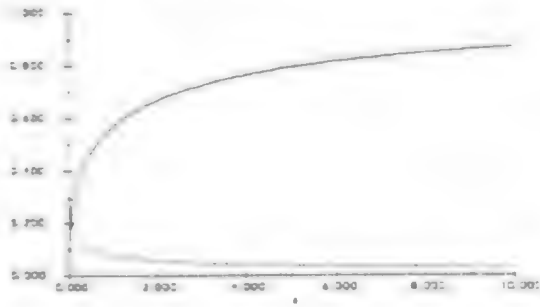
When the ratio of k to U_e and k to A is increased, the conversion is increased.
When these are decreased the conversion decreases.

Use the following POLYMATH program to generate graphs of the conversion and activity profiles for $U_e = 0.025$ m/s, 0.25 m/s, 2.5 m/s, and 25 m/s.

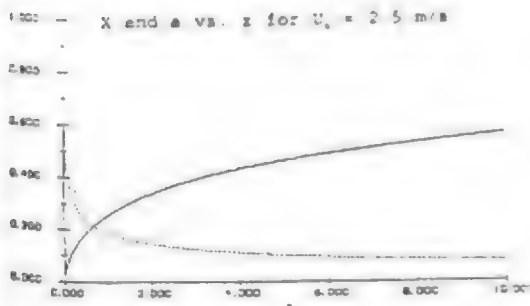
X and a vs z for $U_e = 0.025$ m/s



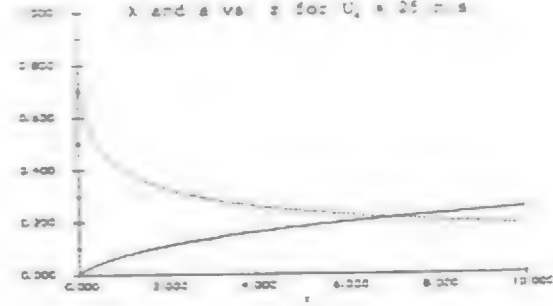
X and a vs z for $U_e = 0.25$ m/s



X and a vs z for $U_e = 2.5$ m/s

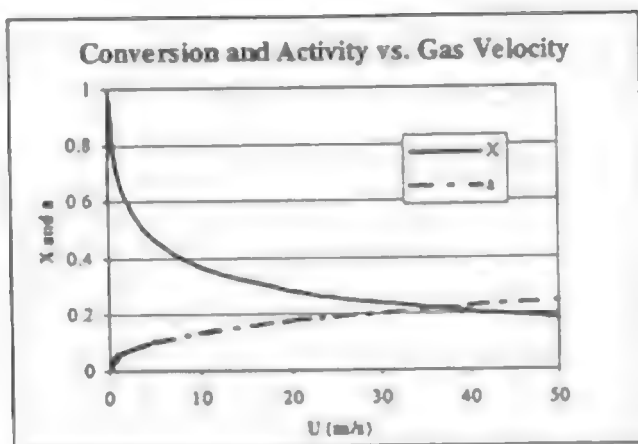


X and a vs z for $U_e = 25$ m/s



It is apparent that as U_e increases, activity increases and conversion decreases.

Use the same program to vary U_e and generate values for the exit conversion and activity. Use these values in Excel to generate the following graph

**P10-3****(a) Surface Rxn Limited**

$$\frac{r_{ADI}}{k_A} = 0 \quad C_{I \cdot S} = K_I C_I C_V \quad C_{W \cdot S} = K_W P_W C_V \quad \frac{r_{ADW}}{k_W} = 0$$

$$\frac{r_D}{k_D} = 0 \quad C_{TBA \cdot S} = \frac{C_{TBA} C_P}{K_D} = K_{TBA} C_{TBA} C_P, \text{ since } \frac{1}{K_D} = K_{TBA}$$

$$r_S = \sqrt{\frac{k}{K_I K_W}} C_V^2 \left[C_I C_W - \frac{C_{TBA}}{K_P} \right] \quad K_P = \frac{K_S K_I K_W}{K_{TBA}}$$

$$C_T = C_V + C_{I \cdot S} + C_{W \cdot S} + C_{TBA \cdot S} = C_V (1 + K_I C_I + K_W C_W + K_{TBA} C_{TBA})$$

$$-r'_I = -r'_W = r'_S = \frac{k \left[C_I C_W - \frac{C_{TBA}}{K_P} \right]}{\left(1 + K_I C_I + K_W C_W + K_{TBA} C_{TBA} \right)^2}$$

(b) Adsorption Isobutene Limited

$$r_{ADI} = k_{AI} \left[C_I - \frac{C_{TBA}}{C_W K_P} \right] C_V \cdot \left(\frac{r_{ADW}}{k_{AW}} \right) = 0 \cdot \left(\frac{r_D}{k_D} \right) = 0$$

$$C_{W \cdot S} = C_W C_V K_W \cdot C_{TBA \cdot S} = C_{TBA} C_V K_{TBA}$$

$$\left(\frac{r'_S}{k_S} \right) = 0 \quad C_{I \cdot S} = \frac{C_V C_{TBA \cdot S}}{C_{W \cdot S} K_S} \quad C_{I \cdot S} = \frac{C_{TBA} K_{TBA} C_V}{C_W K_W K_S}$$

$$r_{ADI} = k_{AI} \left[C_I - \frac{C_{TBA}}{C_W K_P} \right] C_V \quad K_P = \frac{K_W K_S}{K_{TBA}}$$

$$-r'_I = \frac{k_{AI} C_T \left[C_I - \frac{C_{TBA}}{C_W K_P} \right]}{\left[1 + C_W K_W + K_{TBA} C_{TBA} + \frac{C_{TBA}}{C_W K_P} \right]}$$

(c) Eley Rideal Kinetics

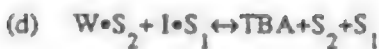
$$r'_S = k_S \left[C_W C_{I \cdot S} - \frac{C_{TBA \cdot S}}{K_S} \right]$$

$$C_{I \cdot S} = K_I C_I C_V$$

$$C_{TBA \cdot S} = K_{TBA} C_{TBA} C_V$$

$$-r'_I = \frac{k \left[C_W C_I - \frac{C_{TBA}}{K_H} \right]}{1 + K_I C_I + K_{TBA} C_{TBA}}, \text{ where } k = k_S K_I C_T \text{ and } K_H = \frac{K_I K_S}{K_{TBA}}$$

P10-3 (cont'd)



$$r_s = k_s \left[C_{W \cdot S_2} C_{I \cdot S_1} - \frac{C_{TBA} C_{V1} C_{V2}}{K_s} \right]$$

$$C_{T1} = C_{V1} + C_{I \cdot S1}$$

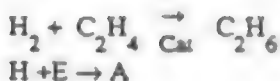
$$C_{T2} = C_{V2} + C_{W \cdot S2}$$

$$C_{I \cdot S1} = K_I C_I C_{V1} \cdot C_{T1} = C_{V1} (1 + K_I C_I)$$

$$C_{W \cdot S2} = K_W C_W C_{V2} \cdot C_{T2} = C_{V2} (1 + K_W C_W)$$

$$r_I = \frac{k \left[C_I C_W - \frac{C_{TBA}}{K_s} \right]}{(1 + K_I C_I)(1 + K_W C_W)}, \text{ where } k = k_s K_W K_I C_{T1} C_{T2}$$

P10-4



Eley Rideal



$$r_s = k_s [C_{E \cdot S} P_H]$$

$$C_T = C_V + C_{E \cdot S}$$

$$r_A = \frac{k}{K_E} C_T \left[\frac{P_E P_H}{1 + K_E P_E} \right]$$

P10-5 A (butanol) \rightleftharpoons B (butene) + C (water)

(a) Possible mechanism:



$$r_{AA} = K_{AA} \left(P_A C_S - \frac{C_{AS}}{K_{AA}} \right)$$

$$r_S = k_S (C_{AS} C_S - C_{BS} C_{CS} / K_S)$$

$$r_{DB} = k_{DB} (C_{BS} - P_B C_S / K_{DB})$$

$$r_{DC} = k_{DC} (C_{CS} - P_C C_S / K_{DC})$$

Assume surface reaction controlling:

$$\frac{-r_{AA}}{k_{AA}} \equiv 0$$

$$C_{AS} = P_A K_{AA} C_S$$

$$\frac{-r_{DB}}{k_{DB}} \equiv 0$$

$$C_{BS} = \frac{P_B C_S}{K_{DB}} = P_B K_{AB} C_S$$

$$\frac{-r_{DC}}{k_{DC}} \equiv 0$$

$$C_{CS} = \frac{P_C C_S}{K_{DC}} = P_C K_{AC} C_S$$

$$-r'_A = r_S = k_S \left(P_A K_{AA} C_S^2 - \frac{P_B P_C C_S^2}{K_S K_{DB} K_{DC}} \right) = k_S K_{AA} C_S^2 \left(P_A - \frac{P_B P_C}{K_{eq}} \right) \text{ where } K_{eq} = K_S K_{AA} K_{DC} K_{DB}$$

$$\text{site balance: } C_T = C_S + C_{AS} + C_{BS} + C_{CS} = C_S (1 + K_{AA} P_A + K_{AB} P_B + K_{AC} P_C)$$

$$\therefore -r'_A = \frac{k_S K_{AA} C_T^2 (P_A - P_B P_C / K_{eq})}{(1 + P_A K_{AA} + P_B K_{AB} + P_C K_{AC})^2}$$

If $P_{B0} = 0$ and $P_{C0} = 0$. then

$$-r'_{A0} = \frac{k_S K_{AA} C_T^2 P_{A0}}{(1 + P_{A0} K_{AA})^2} = \frac{k_1 P_{A0}}{1 + k_2 P_{A0}^2 + k_3 P_{A0}}$$

$$\text{where } \begin{cases} k_1 = k_S K_{AA} C_T^2 \\ k_2 = K_{AA}^2 \\ k_3 = 2 K_{AA} \end{cases}$$

This is consistent with the observation.

(b) From the figure,

Point number	1	2	3	4	5	6
$-r'_{A0} \left(\frac{\text{lbmoles}}{\text{hr} \cdot \text{lb cat}} \right)$	0	0.275	0.5	0.77	0.77	0.5
$P_{A0} \text{ (atm)}$	0	4.5	27	54	112	229
$\sqrt{\frac{P_A}{-r_{A0}}}$	-	4.05	6.45	8.14	12.06	21.4

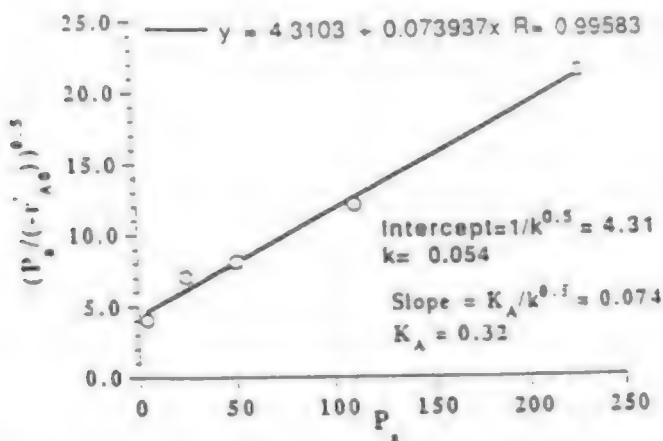
P10-5 (cont'd)

At large P_{A0} : $-r_{A0} = \frac{k_1 P_{A0}}{k_2 P_{A0}^2} = \frac{k_1}{k_2} \left(\frac{1}{P_{A0}} \right)$; using point 6 : $\frac{k_1}{k_2} = (229) (0.5) = 114$

At small P_{A0} : $-r_{A0} = k_1 P_{A0}$; using point 2 : $k_1 = 0.061 \Rightarrow k_2 = 5.34 \times 10^{-4}$

$$-r_{A0} = \frac{0.061 P_{A0}}{1 + 5.34 \times 10^{-4} P_{A0}^2 + k_3 P_{A0}} ; \text{ so } k_3 = \frac{0.061}{-r_{A0}} \cdot \frac{1}{P_{A0}} = 5.34 \times 10^{-4} P_A$$

Using point 3: $k_3 = 7.05 \times 10^{-2}$
 Using point 4: $k_3 = 3.19 \times 10^{-2}$
 Using point 5: $k_3 = 1.05 \times 10^{-2}$ } $\Rightarrow k_3 = 3.19 \times 10^{-2}$
 (The reason for the different values of k_3 is from reading the graph)



c) Find the percent of vacant sites.

$$\% \text{vacant} = \frac{C_T}{C_T} = \frac{C_S}{C_S(1 + K_{AA}P_A + K_{AB}P_B + K_{AC}P_C)}$$

P_B and $P_C = 0$ so that reduces to:

$$\% \text{vacant} = \frac{1}{1 + K_{AA}P_{A0}} = \frac{1}{1 + 0.01596 \cdot 90} = 0.41$$

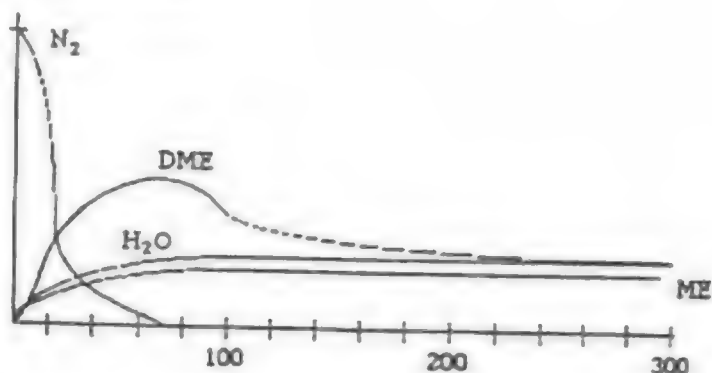
Find the percent of sites occupied by A and B. No B will have occupied any sites at $X = 0$. So:

$$\%A = \frac{K_{AA}P_A}{1 + K_{AA}P_A} = \frac{0.01595 \cdot 90}{1 + 0.01595 \cdot 90} = 0.59$$

d) No solution will be given.

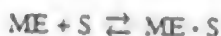
10-14

P10-6



The rate of formation of DME is greater initially. This is a result of more vacant sites being initially available for reaction because water is not adsorbed on the sites. As time goes on the equilibrium concentration of water sites is reached. Water is strongly adsorbed on this catalyst.

Probable Mechanism



Assume Surface Reaction Controls

$$r_s = k_s C_{\text{ME} \cdot \text{S}}^2$$

$$C_{\text{ME} \cdot \text{S}} = K_{\text{ME}} P_{\text{ME}} C_v$$

$$C_{\text{W} \cdot \text{S}} = K_{\text{W}} P_{\text{W}} C_v$$

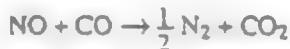
$$r'_{\text{ME}} = r_s = \frac{k P_{\text{ME}}^2}{(1 + K_{\text{W}} P_{\text{W}} + K_{\text{ME}} P_{\text{ME}})^2} \quad \text{where } k = k_s K_{\text{ME}}^2 C_v^2$$

P10-7

Given: Kinetic rate expression for the reduction of NO over a solid catalyst:

$$r = \frac{k P_N P_C}{(1 + K_1 P_N + K_2 P_C)^2} \quad \begin{array}{l} P_N = \text{partial pressure NO} \\ P_C = \text{partial pressure CO} \end{array}$$

Assume that overall reaction is of the form



(a) It is seen that neither N_2 or CO_2 appear in the denominator. This infers that neither is adsorbed on the catalyst. On the other hand, it can be inferred that both NO and CO are adsorbed on the surface. The squared denominator suggests a dual site surface reaction of the adsorbates of NO and CO. Therefore the following mechanism is proposed.



With the surface reaction controlling

$$\frac{-r_{AN}}{k_{AN}} \equiv 0 \quad C_{\text{NO} \cdot \text{S}} = K_{AN} P_N C_S$$

$$\frac{-r_{CN}}{k_{CN}} \equiv 0 \quad C_{\text{CO} \cdot \text{S}} = K_{CN} P_C C_S$$

$$\text{Then } C_T = C_S + C_{\text{NO} \cdot \text{S}} + C_{\text{CO} \cdot \text{S}} = C_S [1 + K_{AN} P_N + K_{CN} P_C]$$

$$\text{and therefore reaction is } -r_S = k_S C_{\text{NO} \cdot \text{S}} C_{\text{CO} \cdot \text{S}} = k_S C_S^2 P_N P_C K_{AN} K_{CN}$$

$$\text{or } -r_S = \frac{k_S K_{AN} K_{CN} P_N P_C C_T^2}{[1 + K_{AN} P_N + K_{CN} P_C]^2} \quad \text{with} \quad \begin{array}{l} k_1 = k_S C_T^2 K_{AN} K_{CN} \\ K_1 = K_{AN} \\ K_2 = K_{CN} \end{array}$$

$$-r_S = \frac{k_1 P_C P_N}{[1 + K_1 P_N + K_2 P_C]^2}$$

(b) Assume that $P_C \gg P_N$. Then P_C changes very little during the course of the reaction and remains constant. A maximum in $(-r_S)$ then occurs, for a fixed value of P_N at:

P10-7 (cont'd)

$$\frac{\partial(-r_s)}{\partial P_C} = \frac{k_1 P_N}{[1 + K_1 P_N + K_2 P_C]^2} - \frac{2 k_1 P_C P_N K_2}{[1 + K_1 P_N + K_2 P_C]^3} = 0$$

$$\text{or at } P_C = \frac{1 + K_1 P_N}{K_2}$$

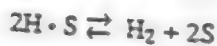
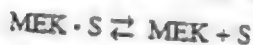
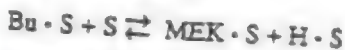
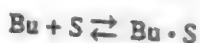
The rate of reaction will increase with an increase in P_C until the above value is reached, after which it will decrease. It appears that there is an excess pressure which will minimize reactor volume. Operating at excess pressure greater than this value will decrease $(-r_s)$, and hence increase V . This analysis is exact if the catalytic reactor is a CSTR. If the reactor is treated as PFR, the critical value of P_C is only approximate, but the general observation is qualitatively the same.

This analysis further assumes that the excess CO can be eliminated easily and economically downstream from the NO converter.

c) The conditions for which the rate law and mechanism are consistent are the following. The CO S surface reaction must be the rate limiting. P_{CO}/P_{NO} must be small. The mechanism must be a dual site mechanism (which it is).

P10-8

(a) From the data we see that H_2 and MEK are weakly adsorbed and the rate goes through a maximum wrt butanol. This maximum suggests a dual site mechanism



$$r_{Bu} = r_{MEK} = \frac{k P_{Bu}}{(1 + K_{Bu} P_{Bu})^2}$$

The partial pressures of MEK and H_2 do not appear in the denominator because they are assumed to be weakly adsorbed.

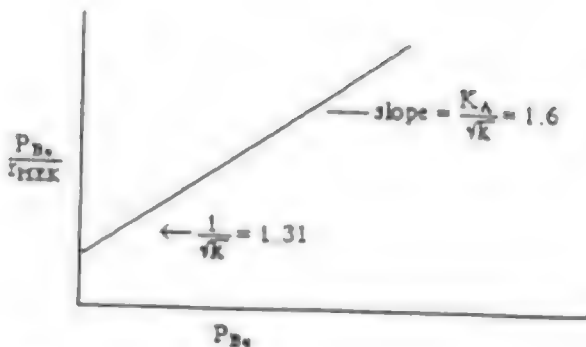
(b)

$$\sqrt{\frac{P_{B_0}}{r_{MEK}}} = \frac{1}{\sqrt{k}} + \frac{K_{B_0}}{\sqrt{k}} P_{B_0}$$

Mole Balance on differential reactor

$$W = \frac{F_{MEK}}{r_{MEK}}$$

P_{B_0}	$\sqrt{\frac{P_{B_0}}{r_{MEK}}}$
2	6.74
0.1	1.59
.5	2.69
1	4.08
2	6.82
1	4.12



$$k = 0.58 \frac{\text{mol}}{\text{hr g} \cdot \text{cal}} \cdot K_A = 2.1 \text{ atm}^{-1}$$

$$-r'_A = -r'_{BW} = \frac{0.58 P_A}{(1 + 2.1 P_A)^2} \frac{\text{mol}}{\text{hr g} \cdot \text{cal}}$$

(c)

Design Equation : $\frac{dX}{dW} = \frac{-r'_A}{F_{A_0}}$

Rate Law : $-r'_A = \frac{k P_A}{(1 + K_A P_A)^2}$ $\epsilon = 1$

Stoichiometry : $P_A = C_A RT = C_{A_0} \left(\frac{1-X}{1+\epsilon X} \right) \frac{P}{P_0} RT \Rightarrow P_A = P_{A_0} \left(\frac{1-X}{1+X} \right)$

Use these equations in POLYMATH to find the catalyst weight necessary to achieve 90% conversion.

$$W = 21.8 \text{ kg}$$

- (d) Use this same POLYMATH program to generate the desired graph:

No pressure change

Equations:

$$d(x)/d(w) = -r_a/f_{a0}$$

$$p_{a0} = 10$$

$$f_{a0} = 600$$

$$k_a = 2.1$$

$$p_a = p_{a0} \cdot ((1-x)/(1+x))$$

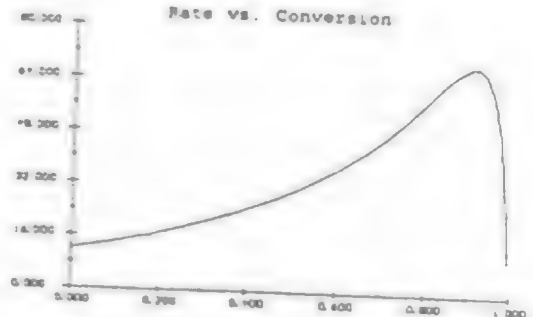
$$r_a = -580 \cdot p_a / (1 + k_a \cdot p_a)^{0.5}$$

$$\text{rate} = -r_a$$

$$w_0 = 0, \quad w_f = 23$$

Initial value

0



- (e) Now consider the change in pressure:

Stoichiometry:
$$P_A = C_A RT = C_{A0} \left(\frac{1-X}{1+\epsilon X} \right) \frac{P}{P_0} RT \Rightarrow P_A = P_{A0} \left(\frac{1-X}{1+X} \right) y$$

Pressure:
$$\frac{dy}{dW} = \frac{-\alpha}{2y} (1+X)$$

Use these new equations in POLYMATH to find that the same amount of catalyst would be required. $W = 21.8 \text{ kg}$

Pressure Change

Equations:

$$d(x)/d(w) = -r_a/f_{a0}$$

$$d(y)/d(w) = -\alpha \cdot (1+x)/2y$$

$$p_{a0} = 10$$

$$f_{a0} = 600$$

$$k_a = 2.1$$

$$\alpha = 0.03$$

$$p_a = p_{a0} \cdot ((1-x)/(1+x))$$

$$r_a = -580 \cdot p_a / (1 + k_a \cdot p_a)^{0.5}$$

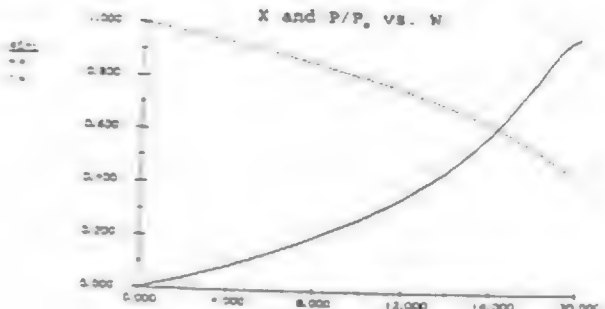
$$\text{rate} = -r_a$$

$$w_0 = 0, \quad w_f = 23$$

Initial value

0

1



P10-9Iso-octene + Hydrogen \rightarrow iso-octane

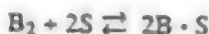
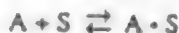
(a) Discrimination of models:

$$\text{Assume } -r_A = k C_A^\alpha C_B^\beta C_C^\gamma$$

For runs 2 and 3, $0 < \alpha < 1$; 2 and 4, $0 < \beta < 1$; and 2 and 5, $-1 < \gamma < 0$. From

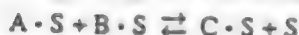
Perry's handbook, 5th ed., p. 4-8; the reaction is probably surface reaction rate controlling.

Mechanism I (H. Alvord):



$$\text{Hence, } -r_A = \frac{k [P_A P_B - P_C / K_{eq}]}{[1 + K_A P_A + K_B^2 P_B^2 + K_C P_C]^2}$$

Mechanism II (S. L. Mullick):



$$\text{Hence, } -r_A = \frac{k [P_A P_B - P_C / K_{eq}]}{[1 + K_A P_A + K_B P_B + K_C P_C]^2}$$

From runs 2, 9 11, 12, $P_A = P_B = P_C = P$, a plot of $-r_A$ vs. P shows a parabolic behavior, therefore we will drop the second term in the denominator for easy linearization.

The readers can calculate K_{eq} value by Gibbs free energy change in this equation (up to 650 K, the reverse reaction is negligible)

The linearized regression model is:

$$\left(\frac{P_A P_B}{-r_A} \right)^{0.5} = \frac{1}{k^{0.5}} + \frac{K_A P_A}{k^{0.5}} + \frac{K_B P_B}{k^{0.5}} + \frac{K_C P_C}{k^{0.5}} = y$$

Using given 12 data points to solve for these four unknowns:

$$y = 3.0 + 1.42 P_A + 0.97 P_B + 1.42 P_C$$

The final results are:

$$-r_A = \frac{0.1113 P_A P_B}{(1 + 0.475 P_A + 0.322 P_B + 0.414 P_C)^2}$$

The comparison of the percentage error between the model and the experimental data are:

Run	P _A	P _B	P _C	r (exp.)	$\left(\frac{P_A P_B}{r_{exp.}}\right)^{0.5}$	r (calc.)	% error
1	1	1	0	0.0362	5.26	0.0345	-4.8
2	1	1	1	0.0239	6.47	0.0227	-4.7
3	1	3	1	0.0390	8.77	0.0410	+5.0
4	3	1	1	0.0351	9.25	0.0334	-4.8
5	1	1	3	0.0114	9.37	0.0120	+5.7
6	1	10	0	0.0534	13.69	0.0505	-5.4
7	10	1	0	0.0310	17.96	0.0302	-2.6
8	1	1	2	0.0033	10.41	0.00315	-4.5
9	2	2	2	0.0380	10.26	0.0380	0
10	0.2	0.2	0.2	0.0032	3.54	0.00288	-9.8
11	0.1	0.1	0.1	0.0008	3.54	0.00089	+10.7
12	5	5	5	0.0566	21.02	0.0599	-1.2

$$\text{sum} = 59.2$$

$$\text{avg.} = 4.9$$

(b) Discussion: The readers may check the validity of mechanism I. To reduce the accumulation of error in calculations, the readers should have used all data points and solved all unknowns simultaneously. To get the maximum information of complex kinetics of a reaction from the least runs, it is advantageous to do planned experiments such as factorial design. (W. G. Hunter, and A. C. Atkinson, Chemical Engineering, p. 159, June 6, 1966).

A paper discussing chemical reaction rate equations from experimental data is in: C. H. Ware Jr., Summer Computer Simulation Conference, Proceedings, 1975, Part I, p. 368.

$$-r_A' = \frac{0.2223 C_{A0}^2 (RT)^2 (1-X)^2 / (1-0.5X)^2}{\left[1 + \frac{C_{A0} RT}{1-0.5X} \{ (0.475 + 0.322 (1-X)) + 0.414 X \} \right]^2}$$

$$-r_A = \frac{0.1113 (RT C_{A0})^2 (1-X)^2 / (1-0.5X)^2}{\left[1 + \frac{C_{A0} RT}{1-0.5X} (0.797 - 0.383 X) \right]^2}$$

$$P_{A0} = C_{A0} RT = 1.5 \text{ atm}$$

$$F_{A0} = 2.5 \frac{\text{mol}}{\text{min}} = 150 \frac{\text{mol}}{\text{hr}}$$

P10-9 (cont'd)

$$\text{CSTR : } W = \frac{150 \times 0.8}{\frac{0.1113 (1.5)^2 (1 - 0.8)^2 / (1 - 0.5 \times 0.8)^2}{\left[1 + \frac{1.5}{1 - 0.5 \times 0.8} (0.797 - 0.383 \times 0.8)^2 \right]}}$$

$$W = 21,380 \text{ g} = 21.4 \text{ kg}$$

$$\text{PFR : } W = F_{A0} \int_0^X \frac{dX}{-r_A}$$

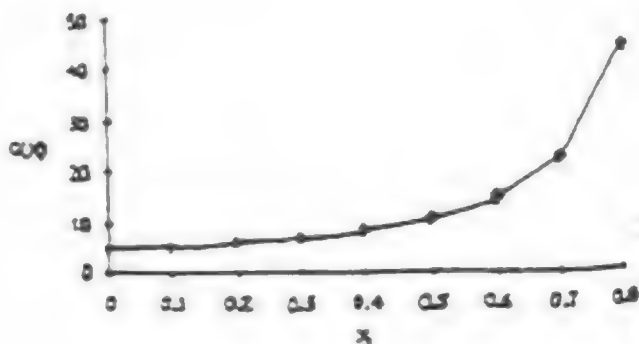
$$W = 150 \int_0^X \frac{dX}{\frac{0.1113 (1.5)^2 (1 - X)^2 / (1 - 0.5 X)^2}{\left[1 + \frac{1.5}{1 - 0.5 X} (0.797 - 0.383 X)^2 \right]}}$$

$$W = \frac{150}{0.1113 \times 2.25} \int_0^X G(X) dX$$

$$\text{where } G(X) = \frac{\left[1 + \frac{1.5 (0.797 - 0.383 X)^2}{1 - 0.5 X} \right]^2 (1 - 0.5 X)^2}{(1 - X)^2}$$

$$G(X) = \frac{(2.1955 - 1.0745 X)^2}{1 - X}$$

X	G(X)
0	4.82
0.1	5.38
0.2	6.13
0.3	7.16
0.4	8.66
0.5	11.00
0.6	15.03
0.7	23.15
0.8	44.62



Using Simpson's rule.

area under the curve = 10

$$W = \frac{150}{0.1113 \times 2.25} \times 10 = 6000 \text{ g} = 6 \text{ kg}$$

10-22

P10-9 (cont'd)

(d) Consider the differential section between L and $L + dL$

In - Out + Generation = Accumulation

$$r_A(C_A, L) A_T \rho_c (1 - \phi) dL = -dL \left[\frac{d}{dL} A_T \psi(L) C_A(L) \right]$$

But: $A_T \psi(L) C_A(L) = N_A(L) = F_{A0}(1 - X)$

$$\therefore F_{A0} \frac{dX}{dL} = TA \rho_c (1 - \phi) r_A(P_i)$$

Relating the expression r_A to X and L :

$$F_A = F_{A0}(1 - X) = \frac{1}{2} F_0 (1 - X)$$

$$F_B = F_{B0}(1 - X) = \frac{1}{2} F_0 (1 - X)$$

$$F_T = \frac{1}{2} (2 - X)$$

$$F_C = F_{A0} X = \frac{1}{2} F_0 X$$

$$P_A = \frac{F_A}{F_T} = \frac{1 - X}{2 - X}$$

$$P_A = P_A = \frac{1 - X}{2 - X} P_T ; P_C = \frac{X}{2 - X} P_T$$

Let $P = P_T$.

$$\frac{dX}{dL} = \frac{TA \rho_c (1 - \phi)}{F_{A0}} r_A \left[\frac{1 - X}{2 - X} P, \frac{1 - X}{2 - X} P, \frac{X}{2 - X} P \right]$$

From the Ergun equation, we have:

$$\frac{dP}{dL} = \frac{G}{\rho_{g0} D_p} \left(\frac{1 - \phi}{\phi^3} \right) \left[\frac{150 (1 - \phi) \mu}{D_p} + 1.75 G \right]$$

All the things on RHS are constant, except for ρ

$$\rho = \rho_0 \left(\frac{P}{P_0} \right) \left(\frac{2}{2 - X} \right)$$

$$\frac{dP}{dL} = \frac{2 - X}{2} \left(\frac{P_0}{\rho_0} \right) \left(\frac{1}{P} \right) \frac{G}{g_c D_p} \left(\frac{1 - \phi}{\phi^3} \right) \left[\frac{150 (1 - \phi) \mu}{D_p} + 1.75 G \right]$$

$$\frac{dP}{dL} = \frac{2 - X}{2P} \beta_0 \text{ where } \beta_0 = \frac{P_0 G}{\rho_0 g_c D_p} \frac{(1 - \phi)}{\phi^3} \left[\frac{150 (1 - \phi) \mu}{D_p} + 1.75 G \right]$$

Let $L^* = \frac{L}{L_{\text{des}}} ; P^* = \frac{P}{P_0}$. then: $\frac{dP}{dL} = \frac{2 - X}{2P^*} \beta_0^*$

where $\beta_0^* = \frac{L_{\text{des}}}{P_0^2} \beta_0$

P10-9 (cont'd)

$$\beta_o = \frac{LG(1-\phi)}{P_o \rho_o g_c D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.75 G \right]$$

$$\phi = 0.4$$

$$D_p = \left(\frac{1}{16} \text{ in} \right) \left(\frac{1 \text{ ft}}{12 \text{ in}} \right) = \frac{1}{192} \text{ ft}$$

$$g_c = 32.174 \frac{\text{lbm} \cdot \text{ft}}{\text{lbf} \cdot \text{sec}^2}$$

$$G = \frac{(F_{A0} m_A + F_{B0} m_B)}{AT} = \frac{\left(150 \frac{\text{gmol}}{\text{hr}} \right) (2 + 112) \frac{\text{g}}{\text{gmol}} \left(\frac{\text{lb}}{453.6 \text{ g}} \right)}{\pi \left(\frac{0.957}{12} \right)^2 \text{ ft}^2}$$

$$G = \frac{7546.9}{\pi} \frac{\text{lbm}}{\text{ft}^2 \cdot \text{hr}}$$

$$P_o = (3 \text{ atm}) \left(\frac{14.7 \text{ psi}}{1 \text{ atm}} \right) \left(\frac{144 \text{ in}^2}{1 \text{ ft}^2} \right) = 6348.7 \frac{\text{lb}}{\text{ft}^2}$$

$$\rho_o = C_T \bar{m} = \left(\frac{57 \text{ lb}}{\text{lbmol}} \right) \frac{P}{RT} = \frac{\left(57 \frac{\text{lb}}{\text{lbmol}} \right) (3 \text{ atm})}{\left(0.7301 \frac{\text{ft}^3 \cdot \text{atm}}{\text{lbmol} \cdot ^\circ \text{R}} \right) [(200 + 273.15)(1.8)] ^\circ \text{R}}$$

$$\rho_o = 0.2750 \frac{\text{lbm}}{\text{ft}^3}$$

$$\left. \begin{aligned} \mu(3 \text{ atm}, 200^\circ \text{C}) &= 9.4719 \times 10^{-3} \text{ cp} \left(\frac{1}{2} C_8, \frac{1}{2} H_C \right) \\ &= 8.6211 \times 10^{-3} \text{ cp (all } C_8) \end{aligned} \right\} \text{ PPROP}$$

$$\Rightarrow \mu = \frac{(9.4719 \times 10^{-3} + 8.6211 \times 10^{-3})}{2} \text{ cp} = 6.7197 \times 10^{-4} \frac{\text{lbm}}{\text{ft} \cdot \text{sec} \cdot \text{cp}} \times \frac{3600 \text{ sec}}{\text{hr}}$$

$$\mu = 0.02188 \frac{\text{lbm}}{\text{ft} \cdot \text{hr}}$$

$$\beta_o = \frac{(35 \text{ ft}) \left(\frac{7546.9}{\pi} \frac{\text{lbm}}{\text{ft}^2 \cdot \text{hr}} \right) (1 - 0.4) \left(\frac{1 \text{ hr}}{3600 \text{ sec}} \right)^2}{\left(6348.7 \frac{\text{lbf}}{\text{ft}^2} \right) \left(0.2750 \frac{\text{lbm}}{\text{ft}^3} \right) \left(32.174 \frac{\text{lbm} \cdot \text{ft}}{\text{lbf} \cdot \text{sec}^2} \right) \left(\frac{1 \text{ ft}}{192} \right) (0.4)^3} \times \left[\frac{150(1 - 0.4) \left(0.02188 \frac{\text{lbm}}{\text{ft} \cdot \text{hr}} \right)}{\left(\frac{1}{192} \text{ ft} \right)} + 1.75 \left(\frac{7546.9}{\pi} \frac{\text{lbm}}{\text{ft}^2 \cdot \text{hr}} \right) \right]$$

10-24

P10-9 (cont'd)

$$\frac{dX}{dL} = \left[\frac{L_d A T \rho_C (1-\phi)}{F_{A0}} \right] R_A(X, P^*)$$

$$\text{where } R_A = \frac{k P_A P_B}{(1 + K_A P_A + K_B P_B + K_C P_C)^2}$$

$$R_A = \frac{K P_o^2 \left(\frac{1-X}{2-X} \right)^2 P^{*2}}{\left[1 + (K_A P_o + K_B P_o) \left(\frac{1-X}{2-X} \right) P^* + K_C P_o \left(\frac{X}{2-X} \right) P^* \right]^2}$$

$$R_A = \frac{K P_o^2 (1-X)^2}{P_o^2 \left[\frac{1}{P_o^2 P^{*2}} + (K_A + K_B) \left(\frac{1-X}{2-X} \right) + K_C \left(\frac{X}{2-X} \right) \right]^2}$$

$$R_A = \frac{K P_o^2 (1-X)^2}{\left[\frac{2-X}{P^{*2}} + (K_A + K_B) P_o (1-X) + K_C P_o X \right]^2}$$

$$\text{Let } \alpha^* = \frac{L A T \rho_B (1-\phi) K P_o^2}{F_{A0}} ; K_1^* = (K_A + K_B) P_o ; K_2^* = (K_C - K_A - K_B) P_o$$

$$\text{Then: } \frac{dX}{dL} = \alpha^* \frac{(1-X)^2}{\left[\frac{2-X}{P^*} + K_1^* + K_2^* X \right]^2}$$

For a given T, we can solve the two ODE's to get X(L*). We need to guess T until X = 0.8.
For the rate constants, we use the solution of 6.10 (a)

$$K = 0.1118 \frac{\text{gmol}}{\text{gcat} \cdot \text{hr} \cdot \text{atm}^2} ; K_A = 0.475 \text{ atm}^{-1} ; K_B = 0.322 \text{ atm}^{-1}$$

$$K_C = 0.414 \text{ atm}^{-1}$$

$$\therefore K_1^* = (0.475 + 0.322) 3 = 2.391$$

$$K_2^* = (0.414 - 0.475 - 0.332) 3 = -1.149$$

$$\alpha^* = \frac{L A T \rho_B (1-\phi) K P_o^2}{F_{A0}} = \frac{T (35 \text{ ft}) (3.14/4) \left(\frac{0.957}{12} \right)^2 \text{ ft}^2 \left(2.6 \frac{\text{g}}{\text{cm}^3} \right)}{\left(25 \frac{\text{gmol}}{\text{min}} \right) \left(\frac{60 \text{ min}}{1 \text{ hr}} \right)}$$

$$\times \left(0.113 \frac{\text{gmol}}{\text{gcat} \cdot \text{hr} \cdot \text{atm}^2} \right) (3 \text{ atm})^2 \left(\frac{30.41 \text{ cm}}{\text{ft}} \right)$$

$$\alpha^* = 85.958 T$$

10-25

P10-9 (cont'd)

$$\beta_o^* = \left(\frac{6.531}{T} \times 10^{-4} \frac{\text{ft}^2 \text{hr}}{\text{lbm}} \right) \left(378.09 + \frac{13207}{T} \right) \frac{\text{lbm}}{\text{ft}^2 \text{hr}}$$

$$\beta_o^* = \frac{0.24693}{T} - \frac{8.6255}{T^2}$$

A FORTRAN program is written to solve the equations. The results show that any numbers of tubes sufficient to allow the given flow rates with a positive pressure provides more than enough catalyst for the desired conversion. The problem as stated, therefore has no solution. However, we can choose a different L , and it only changes the dimensionless parameters. With $L = 20$, the problem is still unsolvable.

$$\text{For } L = 10 \text{ ft} \quad T = 2.16 \text{ tubes} \Rightarrow \frac{P}{P_{in}} = 0.46$$

Note: Using the modified program with

$$D_p = \frac{1}{16} \text{ in} \quad \mu = 9.05 \times 10^{-3} \text{ cp}$$

$$L = 10 \text{ ft} \quad A = 2.15 \text{ in}^2$$

$$\Rightarrow X = 0.80 \quad P^* = 0.7537$$

Using 1 1/2 in schedule 80 pipe (I.D. = 1.5 in), $A = 1.76715 \text{ in}^2$ and the length to get $X = 0.8$ is impossible ($P_f < 0$).

With 2 in schedule 80 pipe (I.D. = 1.939 in), $A = 2.952877 \text{ in}^2$

This gives $L = 6.67 \text{ ft}$, $X = 0.80$ and $P = 0.9173$

$$1 \frac{1}{2} \text{ in schedule 40} \Rightarrow A = 2.03580 \text{ in}^2$$

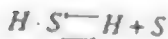
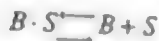
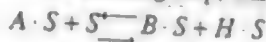
$$L = 10.94857 \quad X = 0.8 \text{ and } P = 0.6903$$

P10-10

a)



Assume a rate-limiting step; start with surface reaction



Assume a rate-limiting step; start with surface reaction

$$-r_A = r_i = k_i C_v P_{A \cdot S}$$

Come up with ways to find $P_{A \cdot S}$, $P_{B \cdot S}$, and $P_{H \cdot S}$.

$$\frac{r_{AD}}{k_{AD}} = 0$$

$$C_{A \cdot S} = K_{AA} P_A C_v$$

$$\frac{r_{BD}}{k_{BD}} = 0$$

$$C_{B \cdot S} = \frac{P_B C_v}{K_{DB}} = K_{AB} P_B C_v$$

$$\frac{r_{HD}}{k_{HD}} = 0$$

$$C_{H \cdot S} = \frac{P_H C_H}{K_{DH}} = K_{DH} P_H C_v$$

Find the expression for C_i .

$$C_i = C_v + C_{A \cdot S} + C_{B \cdot S} + C_{H \cdot S}$$

Combine all of those to get the following rate law suggestion.

$$r_i = \frac{k_i K_A P_A C_i^2}{(1 + K_A P_A + K_B P_B + K_H P_H)^2} = \frac{k P_A}{(1 + K_A P_A + K_B P_B + K_H P_H)^2}$$

Checking to see if it fits, we see that for high P_A , increases in P_A cause decreases in the rate. We see that if P_B or P_H increase the rate will go down, which is consistent with the rate law.

b) Now using POLYMATH's non-linear equation regression we can find the values for the parameters. We find that

$$k = 0.00137$$

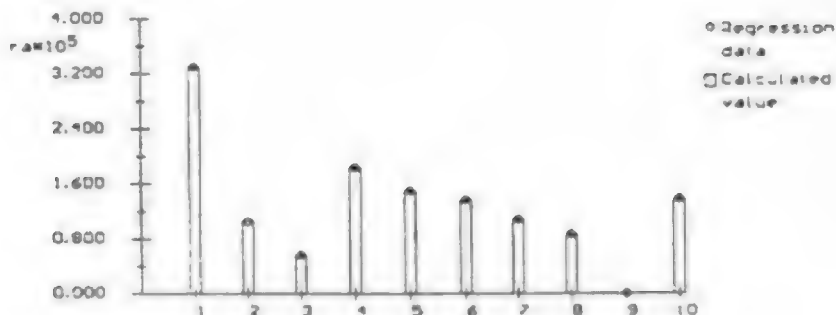
$$K_A = 4.76$$

$$K_B = 0.259$$

$$K_C = 0.424$$

In the problem it is given that K_A is 1 or 2 orders of magnitude greater than K_B and K_C which is true so this is a good answer.

P10-10 (cont'd)



Model: $r_A = k_D a (1 - K_A a P_A - K_B a P_B - K_C a P_C) / (1 + K_A a P_A + K_B a P_B + K_C a P_C)^2$
 $k = 0.00137022$ $K_B = 0.259382$
 $K_A = 4.76084$ $K_C = 0.42358$
 7 positive residuals, 3 negative residuals. Sum of squares = $5.27033e-15$

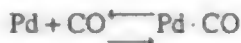
c) No solution will be given.

P10-11

Rate law:

$$-r_{AC} = \frac{k C_{CO} C_{AC} C_{NaOH}}{(1 + K_{AC} C_{AC})^2}$$

Proposed Mechanism:



Neither of the first two reactions can be limiting because they are reversible. The rate step must be irreversible because there is no subtraction function in the numerator.

P10-11 (cont'd)

We will first try the third equation as the rate-limiting step:

$$r_A = k C_v P_{AC}$$

Then

$$C_1 = C_v + C_{Pd \cdot CO} + C_{Pd \cdot CO \cdot NaOH} + C_{Pd \cdot AC}$$

Find equations for $C_{Pd \cdot CO}$, $C_{Pd \cdot CO \cdot NaOH}$, and $C_{Pd \cdot AC}$

$$\frac{r_{ACO}}{k_{ACO}} = 0$$

$$C_{Pd \cdot CO} = C_v C_{CO} K_{CO}$$

$$\frac{r_{ACO \cdot NaOH}}{k_{NaOH}} = 0$$

$$C_{Pd \cdot CO \cdot NaOH} = K_{CO} K_{NaOH} C_v C_{NaOH} C_{CO}$$

$$\frac{r_{AC}}{k_{AC}} = 0$$

$$C_{Pd \cdot AC} = 0$$

Combine to find C_v

$$C_v = \frac{C_1}{1 + C_{CO} K_{CO} + K_{CO} K_{NaOH} C_{NaOH} C_{CO}}$$

This is definitely not what is supposed to be on the bottom of the rate law so reaction 3 can not be rate-limiting.

Trying reaction 4:

$$r_4 = k_4 C_{Pd \cdot AC} C_{Pd \cdot CO \cdot NaOH}$$

$C_{Pd \cdot AC}$ cannot be found so therefore this rate law is also not rate-limiting so none of the mechanisms reactions agree with the rate law.

P10-12

a) Assume that the second reaction is the rate-limiting step.

$$r_s = k_2 C_{SiH_4 \cdot s}$$

Using PSSH, we know that

$$r_{SiH_4 \cdot s} = 0 = k_1 C_{SiH_4 \cdot s} C_v$$

$$C_{SiH_4 \cdot s} = \frac{k_1 C_{SiH_4} C_v}{k_2} = K C_{SiH_4} C_v$$

$$K = \frac{k_1}{k_2}$$

P10-12 (cont'd)

Perform a site balance:

$$C_t = C_v + C_{SiH_4} S$$

$$C_v = \frac{C_t}{1 + KC_{SiH_4}}$$

Combining all of these we find:

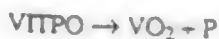
$$r_s = \frac{k_1 C_{SiH_4} C_v}{1 + KC_{SiH_4}} = \frac{k C_{SiH_4}}{1 + KC_{SiH_4}}$$

This rate law is consistent with the data. As the concentration gets larger, the rate change gets smaller which is consistent with the rate law as given.

b) No answer is right or wrong, but the points will probably be higher than the ones given to see that the change in rate becomes even smaller.

P10-13

At low temperature (120°C) the reaction goes from 2nd order to zero order. At high temperatures only second order.



$$\text{Let } VI \equiv VITPO$$



$$\dot{r}_{VO_2} = -\dot{r}_{VI} = r_s = k_s f_{VI}^2$$

$$f_{VI} = K_{VI} P_{VI} f_v$$

$$1 = f_v + f_{VI}$$

$$-\dot{r}_{VI} = \frac{k}{k_s K_{VI}^2 P_{VI}^2} = k \frac{P_{VI}^2}{(1 + K_{VI} P_{VI})^2} = \dot{r}_{VO_2}$$

at high temperature $K_{VI} P_{VI} \ll 1$ and $-\dot{r}_{VI} = k P_{VI}^2$

P10-13 (cont'd)

Lineage

$$\frac{P_{V1}}{\sqrt{-r_{V1}}} = \frac{1}{\sqrt{k}} + \frac{K_{V1}}{\sqrt{k}} P_{V1}$$

$-r_{V1}$	0.004	0.015	0.03	0.06	0.085	0.16
P_{V1}	0.1	0.2	0.3	0.5	0.7	1.1
$(P_{V1}/\sqrt{-r_{V1}})$	1.58	1.63	1.73	2.04	2.40	2.84

$$\text{Intercept} = \frac{1}{\sqrt{k}} = 1.43 \text{ Torr}/(\mu\text{m/hr})^{1/2}$$

$$k = 0.49 \mu\text{m/hr} \cdot \text{Torr}^2$$

$$\text{Slope} = \frac{K_{V1}}{\sqrt{k}} = \frac{2.50 - 1.43}{1} = 1.13/(\mu\text{m/hr})^{1/2}$$

$$K_{V1} = 1.13 \sqrt{k} = \frac{1.13}{1.43}$$

$$K_{V1} = 0.79/\text{Torr}$$

P10-14

$$r_{NO_2} = k_s f_{I,s}$$

$$f_{I,s} = P_I K_I f_v$$

$$1 = f_v + f_{I,s} = f_v (1 + K_I P_I)$$

$$f_{I,s} = \frac{K_I P_I}{1 + K_I P_I}$$

$$\frac{P_I P_{P1}}{P_{TTP}^2} = K_P \quad P_I = K_P P_{TTP}^2 / P_{P1}$$

$$r_{NO_2} = \frac{k_s P_I K_I}{1 + P_I K_I}$$

$$r_{NO_2} = \frac{k P_{TTP}^2 / P_{P1}}{1 + (P_{TTP}^2 / P_{P1}) K} = \frac{k P_{TTP}^2}{P_{P1} + P_{TTP}^2 K}$$

Low P_{TTP} : Rxn is second order

Since $1 \gg K P_{TTP}^2 / P_{P1}$

High P_{TTP} : $1 \ll K P_{TTP}^2 / P_{P1}$

Reaction is zero order

High Temperature K_I very small such that

$$P_{TTP}^2 K_P K_I \ll P_{P1}$$

P10-15

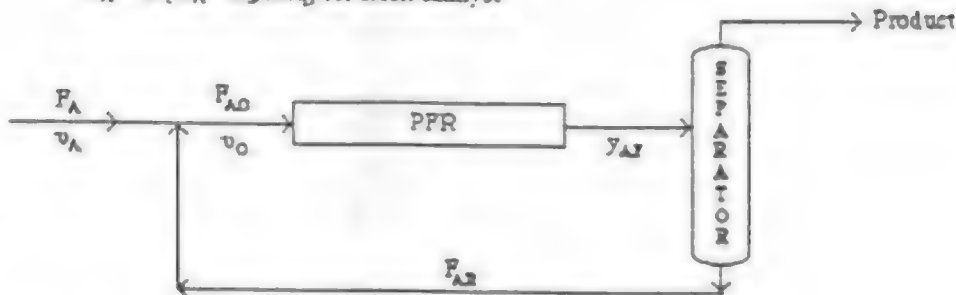
Given: Isomerization reaction $A \rightleftharpoons B$ over a supported catalyst

$$K_{eq} = 8.5 \text{ at } 350^\circ\text{F} = 810^\circ\text{R}$$

$$K_{eq} = 6.0 \text{ at } 400^\circ\text{F} = 860^\circ\text{R}$$

$$E = 26,900 \text{ Btu/lbmol}$$

$$-r_A = k [C_A - C_B/K_{eq}] \text{ for fresh catalyst}$$



$$\theta_B = 0$$

$$\varepsilon = 0$$

Let ρ_o = solution density (constant)

$$(MW)_A = \text{mol. wt.}$$

$$y_{AF} = \frac{\text{mole recycled}}{\text{mole fed}}$$

$$\text{Then } F_{AF} = \frac{y_{AF} \rho_o v_o}{(MW)_A} : F_{AO} = \frac{\rho_o v_o}{(MW)_A}$$

$$\text{Assume total recycle of unreacted A. Then } F_{AR} = F_{AO} = \frac{y_{AO} \rho_o v_o}{(MW)_A}$$

By material balance on the T upstream to the reactor:

$$F_A = F_{AO} - F_{AR} = \frac{\rho_o v_o}{(MW)_A} (1 - y_{AR}) = \frac{\rho_o v_A}{(MW)_A} \Rightarrow v_o = \frac{v_A}{1 - y_{AR}}$$

$$X_{AR} = \frac{F_{AO} - F_{AR}}{F_{AO}} = \frac{\frac{\rho_o v_o}{(MW)_A} (1 - y_{AR})}{\frac{\rho_o v_o}{(MW)_A}} = 1 - y_{AR}$$

Then $-r_A = \alpha k [C_A - C_B / K_C]$ where α = activity

$$C_A = C_{AO}(1-X) : C_B = C_{AO} X : V = F_{AO} \int \frac{dX}{-r_A}$$

P10-15 (cont'd)

$$V = F_{A0} \int_0^{X_{AF}} \frac{dX}{\alpha k [C_A - C_B/K_C]} = \frac{F_{A0}}{\alpha k C_{A0}} \int_0^{X_{AF}} \frac{dX}{\left[1 - \left(1 + \frac{1}{K_C}\right)X\right]}$$

$$\alpha k V = \frac{v_0}{1 + \frac{1}{K_C}} \ln \frac{1}{\left[1 - \left(1 + \frac{1}{K_C}\right)X_{AF}\right]} = \frac{v_A}{(1 - y_{AF})\left(1 + \frac{1}{K_C}\right)} \ln \frac{1}{\left[1 - \left(1 + \frac{1}{K_C}\right)X_{AF}\right]} \quad (a)$$

Case I: Fresh catalyst: $\alpha=1$, $T=350^\circ\text{F}$; $v_A = 310 \frac{\text{gal}}{\text{hr}}$, $y_{AF} = 0.25$

$$\therefore X_{AF} = 1 - y_{AF} = 0.75$$

$$\alpha k_1 V = \frac{310 \text{ gal/hr}}{(0.75)\left(1 + \frac{1}{8.5}\right)} \ln \frac{1}{\left[1 - \left(1 + \frac{1}{8.5}\right)(0.75)\right]} = 674 \frac{\text{gal}}{\text{hr}}$$

Case II: Spent catalyst, $T=400^\circ\text{F}$, $v_A = 300 \frac{\text{gal}}{\text{hr}}$, $y_{AF} = 0.32$

$$\therefore X_{AF} = 1 - y_{AF} = 0.68 \quad \text{By Arrhenius relationship, with:}$$

k_1 = velocity constant at $T_1 = 810^\circ\text{R}$

k_2 = velocity constant at $T_2 = 860^\circ\text{R}$

$$\frac{k_2}{k_1} = \exp \left\{ -\frac{E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right\}$$

$$\therefore k_2 = k_1 \exp \left\{ -\frac{26900 \text{ Btu/lbmol}}{1.987 \text{ Btu/lbmol}^\circ\text{R}} \left(\frac{1}{860^\circ\text{R}} - \frac{1}{810^\circ\text{R}} \right) \right\} = 2.6 k_1$$

From equation (a)

$$\alpha k_2 V = \frac{300 \text{ gal/hr}}{(0.68)\left(1 + \frac{1}{6}\right)} \ln \frac{1}{1 - \left(1 + \frac{1}{6}\right)(0.68)} = 596 \frac{\text{gal}}{\text{hr}}$$

$$\alpha = \frac{596}{k_2 V} = \frac{596}{2.6 k_1 V} = \frac{596}{(2.6)(674)} = 0.340$$

Case III: After ACC regenerative treatment $T=350^\circ\text{F}$; $v_A = 220 \frac{\text{gal}}{\text{hr}}$; $y_{AF} = 0.19$

$$X_{AF} = 1 - y_{AF} = 0.81$$

From equation (a):

$$\alpha k_1 V = \frac{220 \text{ gal/hr}}{(0.81)\left(1 + \frac{1}{8.5}\right)} \ln \frac{1}{\left[1 - \left(1 + \frac{1}{8.5}\right)(0.81)\right]} = 573 \frac{\text{gal}}{\text{hr}}$$

$$\alpha = \frac{573}{k_1 V} = \frac{573}{674} = 0.850 < 0.9$$

\therefore Part (a) of ACC guarantee is not satisfied comparing Case III to Case II

$\frac{\alpha_{III}}{\alpha_{II}} = \frac{0.850}{0.340} = 2.50 > 2.25$ However regenerative technique more than satisfies part (b) of

the ACC guarantee. Therefore the ACC guarantee was met.

10-33

P10-16

a) Mole balance:

$$\frac{dX}{dW} = \frac{(-r'_A)a}{F_{A0}}$$

Rate law:

$$r'_A = -k'C_A$$

Decay law:

$$\frac{da}{dW} = -\frac{k_d a C_A}{U_s}$$

Stoichiometry:

$$C_A = \frac{C_{A0}(1-X)}{(1+\epsilon X)}$$

Evaluate the parameters:

$$\epsilon = .8$$

POLYMATH

Equations:

$$d(x)/d(w) = a*(-ra)/fao$$

$$d(a)/d(w) = -kd*a*ca/Us$$

$$kd=9$$

$$fao=4000000$$

$$Us=250000$$

$$k=90$$

$$cao=.8$$

$$eps=.8$$

$$ca=cao*(1-x)/(1+eps*x)$$

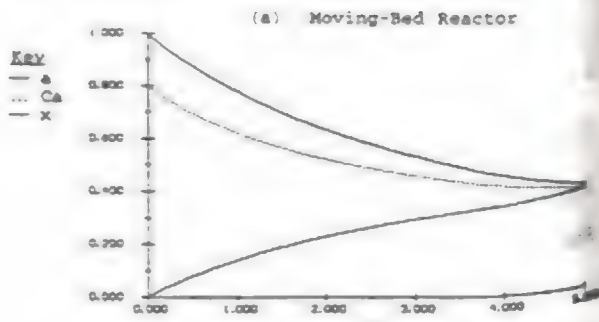
$$ra=-k*ca$$

$$w_0 = 0, \quad w_f = 50000$$

Initial value

0

1



b) Mole balance:

$$\frac{dC_{A1}}{dt} = \frac{C_{A0}}{\tau} - \left(\frac{1 + y_{A0}}{1 + \frac{C_{A1}}{C_{T0}}} + \tau k \right) \frac{C_{A1}}{\tau}$$

$$\frac{dC_{A2}}{dt} = \frac{C_{A1}}{\tau} - \left(\frac{1 + y_{A1}}{1 + \frac{C_{A2}}{C_{T0}}} + \tau k \right) \frac{C_{A2}}{\tau}$$

$$\frac{dC_{A3}}{dt} = \frac{C_{A2}}{\tau} - \left(\frac{1 + y_{A2}}{1 + \frac{C_{A3}}{C_{T0}}} + \tau k \right) \frac{C_{A3}}{\tau}$$

$$\frac{dC_{A4}}{dt} = \frac{C_{A3}}{\tau} - \left(\frac{1 + y_{A3}}{1 + \frac{C_{A4}}{C_{T0}}} + \tau k \right) \frac{C_{A4}}{\tau}$$

$$\frac{dC_A}{dt} = \frac{C_{A4}}{\tau} - \left(\frac{1 + y_{A4}}{1 + \frac{C_A}{C_{T0}}} + \tau k \right) \frac{C_A}{\tau}$$

Everything else is the same and we need to know τ .

$$\tau = \frac{V}{v_0} = 0.004$$

P10-16 (b) 5 CSTR's in Series

Equations:

$$d(a)/d(t) = -k_d \cdot a \cdot ca$$

$$d(ca)/d(t) = ca_4/\tau - ((1 + y_{A4})/(1 + ca_4/cto)) + \tau \cdot a \cdot k \cdot ca/\tau$$

$$d(ca_4)/d(t) = ca_3/\tau - ((1 + y_{A3})/(1 + ca_4/cto)) + \tau \cdot a \cdot k \cdot ca_4/\tau$$

$$d(ca_1)/d(t) = ca_0/\tau - ((1 + y_{A0})/(1 + ca_1/cto)) + \tau \cdot a \cdot k \cdot ca_1/\tau$$

$$d(ca_2)/d(t) = ca_1/\tau - ((1 + y_{A1})/(1 + ca_2/cto)) + \tau \cdot a \cdot k \cdot ca_2/\tau$$

$$d(ca_3)/d(t) = ca_2/\tau - ((1 + y_{A2})/(1 + ca_3/cto)) + \tau \cdot a \cdot k \cdot ca_3/\tau$$

$$kd=9$$

$$\tau=0.004$$

$$cto=1$$

$$k=45$$

$$cao=0.8$$

$$ya_4=ca_4/cto$$

$$ya_1=ca_1/cto$$

$$ya_2=ca_2/cto$$

$$ya_3=ca_3/cto$$

$$x=(cao-ca)/cao$$

$$yao=cao/cto$$

$$t_0 = 0, \quad t_f = 0.5$$

Initial value

1

0.8

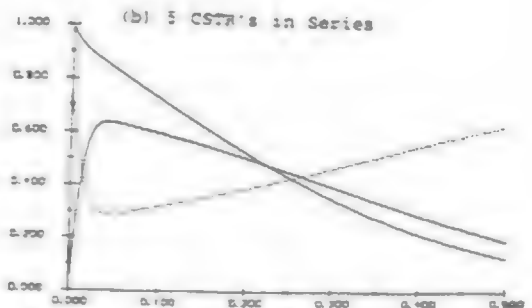
0.8

0.8

0.8

0.8

Key
— a
— Ca
— x



10-35

c) The only change from part (a) is the decay law:

$$\frac{da}{dt} = -k_d a C_A$$

$$t = \frac{W_{max} - W}{U_s}$$

$$dt = \frac{-dW}{U_s}$$

$$\frac{da}{dW} = \frac{k_d C_A a}{U_s}$$

Integrating:

$$\ln a = \frac{k_d C_A W}{U_s} + k$$

$$W = W_{max} @ a = 1$$

$$k = -\frac{k_d C_A W_{max}}{U_s}$$

$$a = \exp\left(\frac{k_d C_A (W - W_{max})}{U_s}\right)$$

Equations:

$$d(x)/d(w) = a \cdot (-r_a) / f_{ao}$$

$$k=90$$

$$f_{ao}=4000000$$

$$k_d=9$$

$$U_s=250000$$

$$w_{max}=50000$$

$$c_{ao}=.8$$

$$\epsilon=.8$$

$$c_a = c_{ao} \cdot (1-x) / (1+\epsilon \cdot x)$$

$$r_a = -k \cdot c_a$$

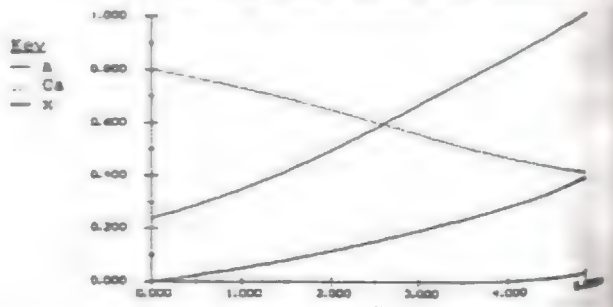
$$a = \exp(k_d \cdot c_a / U_s \cdot (w - w_{max}))$$

$$w_0 = 0, \quad w_f = 50000$$

Initial value

0

(c) Moving-Bed Reactor (Countercurrent)

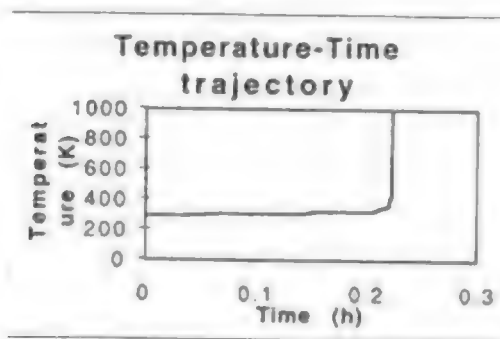


d) To find the Time-Temperature Trajectory we need to use the following equation for first-order decay.

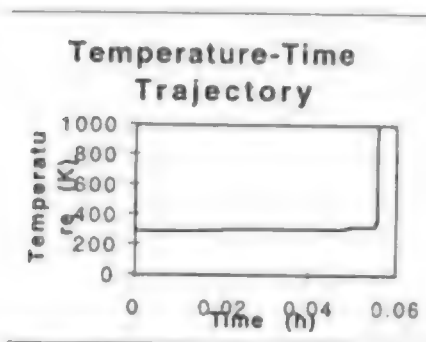
$$t = \frac{E_a}{k_{d0} C_A E_d} \left[1 - \exp\left[\frac{E_d}{R} \left(\frac{1}{T} - \frac{1}{300}\right)\right] \right]$$

P10-16 (cont'd)

Since no initial temperature was given, we assumed one of 300K. This is the graph of that equation.



e) The two energy of activations are switched and this is the new graph made.



The graph looks the same just the time is much smaller.

P10-17

For all of the parts, the mole balances and rate laws are the same. They are:

$$\begin{aligned} \frac{dC_A}{dW} &= r_A v_0 & \frac{dC_B}{dW} &= r_B v_0 \\ r_A &= -k_a C_A & r_B &= k_a C_A \end{aligned}$$

a) Find the equation needed for a.

$$\begin{aligned} -\frac{da}{dt} &= k_a a C_A \\ a &= \exp(-k_a C_A t) \end{aligned}$$

a=1 when t=0

Assuming values for v_0 , k , and k_d come up with the following graphs according to the cases described.

P10-17 (cont'd)

Equations:

$$d(cb)/d(w) = rb \cdot vo$$

$$d(ca)/d(w) = ra \cdot vo$$

$$vo = 10$$

$$a = 1$$

$$kd = 1$$

$$t = 20$$

$$k = 1$$

$$ra = -k \cdot a \cdot ca$$

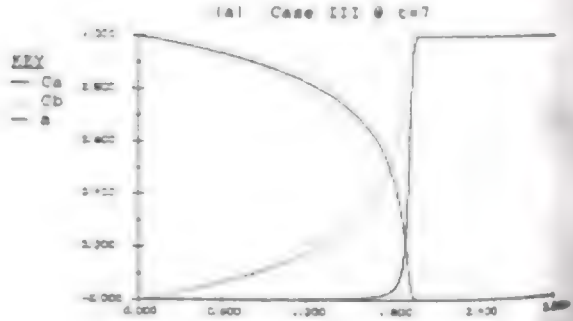
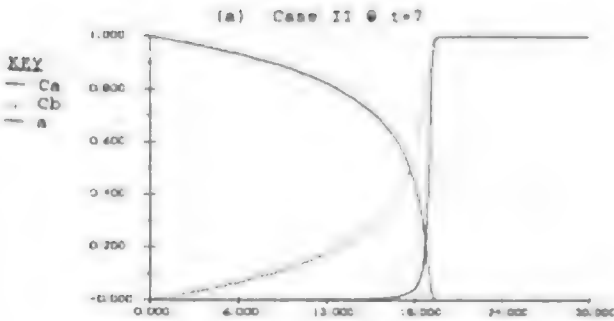
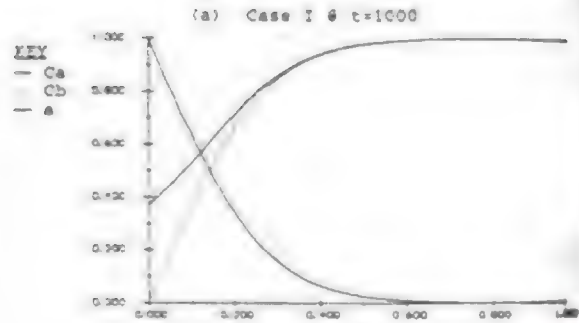
$$rb = k \cdot a \cdot ca$$

$$w_0 = 0, \quad w_f = 50$$

Initial value

$$0$$

$$1$$



b) Find the new equation for a:

$$-\frac{da}{dt} = k_d a^2 C_A$$

$$a = \frac{1}{1 + k_d C_A t}$$

Using same values come up with these graphs:

Equations:

$$d(cb)/d(w) = rb \cdot vo$$

$$d(ca)/d(w) = ra \cdot vo$$

$$vo = 10$$

$$kd = .001$$

$$t = 1000$$

$$k = 1$$

$$a = 1/(1 + kd \cdot ca \cdot t)$$

$$ra = -k \cdot a \cdot ca$$

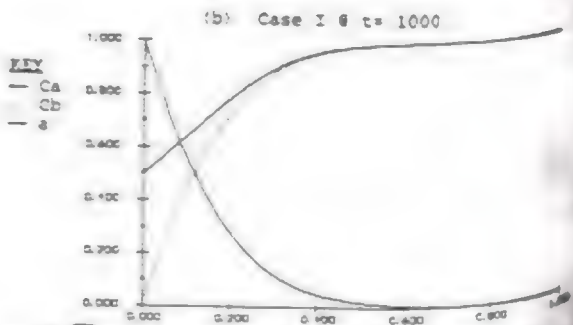
$$rb = k \cdot a \cdot ca$$

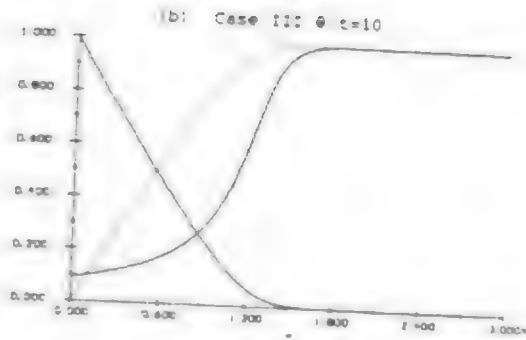
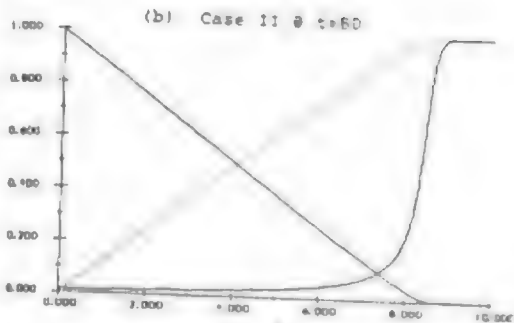
$$w_0 = 0, \quad w_f = 1$$

Initial value

$$0$$

$$1$$





c) Find the new equation for a:

$$-\frac{da}{dt} = k_d a C_b$$

$$a = \exp(-k_d C_b t)$$

The following graphs are made:

Equations:

$$d(Ca)/d(w) = r_a \cdot v_0$$

$$d(Cb)/d(w) = r_b \cdot v_0$$

$$v_0 = 10$$

$$k_d = .001$$

$$t = 1000$$

$$k_{a1}$$

$$a = \exp(-k_d \cdot C_b \cdot t)$$

$$r_b = k \cdot a \cdot C_a$$

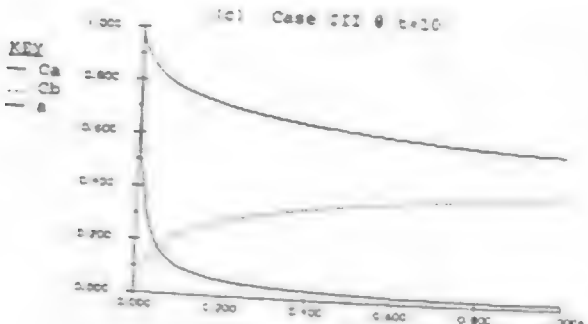
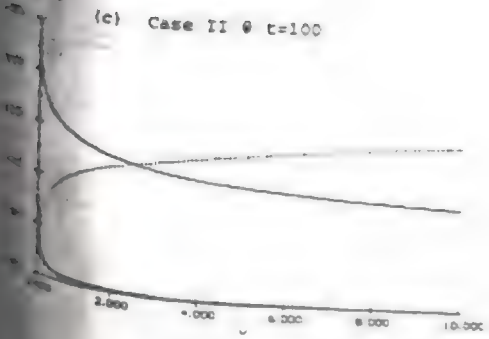
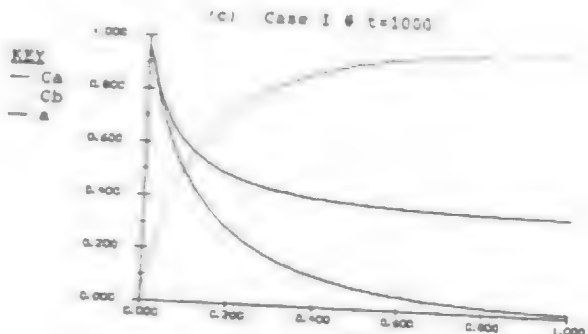
$$r_a = -k \cdot a \cdot C_a$$

$$w_0 = 0, \quad w_f = 1$$

Initial value

1

0



d) Making a into a differential equation we come up with this:

$$-\frac{da}{dt} = k_d C_A a$$

$$t = \frac{W}{U_s}$$

$$-\frac{da}{dW} = \frac{k_d C_A a}{U_s}$$

Equations

$$d(Ca)/d(W) = r_a \cdot v_o$$

$$d(Cb)/d(W) = r_b \cdot v_o$$

$$d(a)/d(W) = -k_d \cdot a \cdot Ca / U_s$$

$$v_o = 10$$

$$k_d = .001$$

$$U_s = 10$$

$$k = 1$$

$$r_b = k \cdot a \cdot Ca$$

$$r_a = -k \cdot a \cdot Ca$$

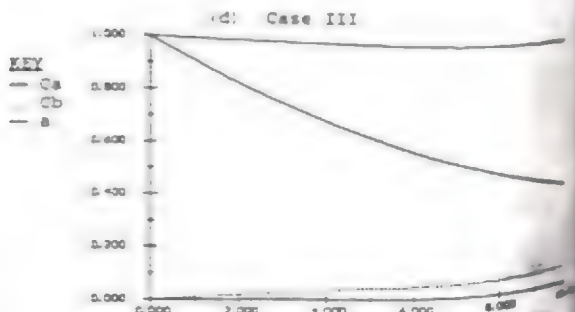
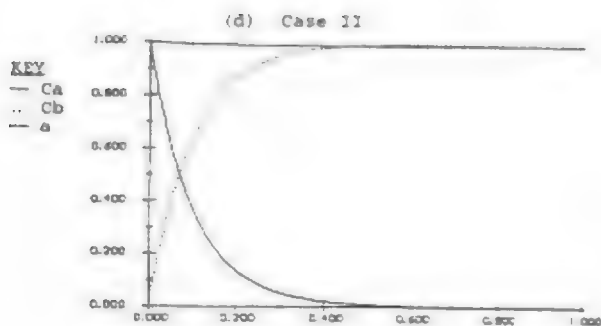
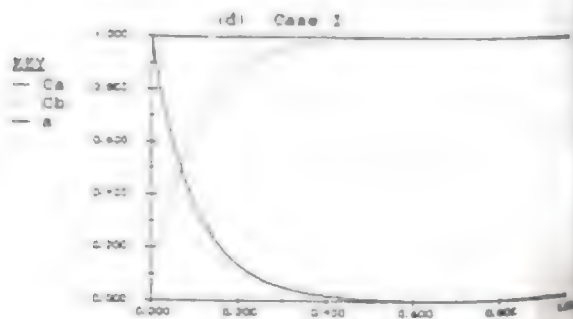
$$w_0 = 0, \quad w_e = 1$$

Initial value

1

0

1



e) Everything from part (d) is the same except for the decay law.

$$\frac{da}{dt} = -k_d a C_A$$

$$t = \frac{W_{MAX} - W}{U_s}$$

$$dt = -\frac{dW}{U_s}$$

$$\frac{da}{dW} = \frac{k_d C_A a}{U_s}$$

Integrating:

$$\ln a = \frac{k_d C_A W}{U_s} + k$$

$$W = W_{MAX} @ a = 1$$

$$k = - \frac{k_d C_A W_{MAX}}{U_s}$$

$$a = \exp \left[\frac{k_d C_A (W - W_{MAX})}{U_s} \right]$$

Equations:

$$d(ca)/d(w) = ra \cdot vo$$

$$d(cb)/d(w) = rb \cdot vo$$

$$vo = 10$$

$$kd = 1$$

$$Us = 10$$

$$k = .001$$

$$wmax = 10$$

$$a = \exp(kd \cdot ca / Us \cdot (w - wmax))$$

$$rb = k \cdot a \cdot ca$$

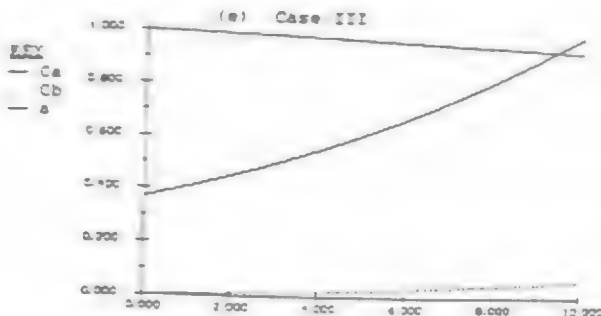
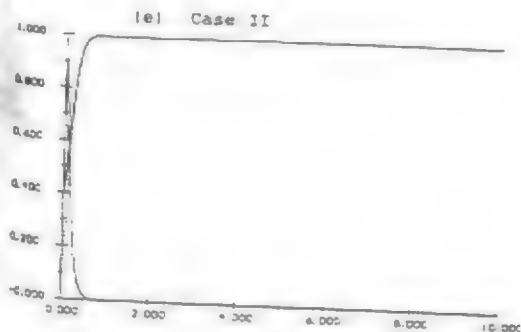
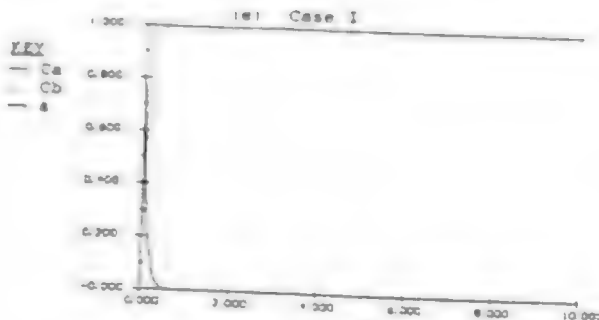
$$ra = -k \cdot a \cdot ca$$

$$w_0 = 0, \quad w_f = 10$$

Initial value

1

0



P10-18

a) Start with a mole balance:

$$\frac{dX}{dW} = \frac{-r'_A}{F_{A0}}$$

Rate law comes next:

$$-r'_A = k_d a$$

Then the decay law:

$$\frac{da}{dt} = -k_d$$

$$t = \frac{W}{U_s}$$

$$\frac{da}{dW} = -\frac{k_d}{U_s}$$

We then come up with the equation for the profit

$$P = 160 \cdot (F_B) - 10 \cdot (U_s)$$

Where:

$$F_B = F_{A0} \cdot X$$

Then plug into POLYMATH and get the following program. The feed rate of solids that gives a maximum profit is 4 kg/min.

10-18a

Equations:

$$d(a)/d(w) = -k_d/U_s$$

$$d(x)/d(w) = -r_a/f_{a0}$$

$$f_{a0} = 1$$

$$k_d = 2$$

$$U_s = 4$$

$$k_r = 1$$

$$r_a = -k_r \cdot a$$

$$f_b = f_{a0} \cdot x$$

$$P = 160 \cdot f_b - 10 \cdot U_s$$

$$w_0 = 0, \quad w_f = 1$$

Initial value

1

0

10-18a

VariableInitial valueMaximum valueMinimum valueFinal value

w

0

1

0

1

a

1

1

0.5

0.5

x

0

0.75

0

0.75

f_{a0}

1

1

1

1

k_d

2

2

2

2

U_s

4

4

4

4

k_r

1

1

1

1

r_a

-1

-0.5

-1

-0.5

f_b

0

0.75

0

0.75

P

-40

80

-40

80

10-42

b) As seen above: $X = 0.75$ and $a = .5$

c) The only equation that changes is the rate law:

$$\frac{da}{dt} = -k_d$$

$$r = \frac{W_{MAX} - W}{U}$$

$$dt = \frac{-dW}{U}$$

$$\frac{da}{dW} = \frac{k_d dW}{U}$$

Integrating we get this:

$$a = \frac{k_d W}{U} + k$$

$$W = W_{MAX} @ a = 1$$

$$k = 1 - \frac{k_d W}{U}$$

$$a = 1 - \frac{k_d (W_{MAX} - W)}{U}$$

Equations:

$$d(x)/d(w) = -ra/ao$$

$$kr=5$$

$$fao=1$$

$$kd=2$$

$$Us=.8$$

$$wmax=1$$

$$fb = \text{if}(x < 1) \text{ then } (fao \cdot x) \text{ else } (1)$$

$$a = \text{if}(kd/Us \cdot (wmax - w) < 1) \text{ then } (1 - kd/Us \cdot (wmax - w)) \text{ else } (0)$$

$$P = 150 \cdot fb - 10 \cdot Us$$

$$ra = a \cdot kr$$

$$w_0 = 0, \quad w_f = 1$$

Initial value

0

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	1	0	1
x	0	1	-8.245e-18	1
kr	5	5	5	5
fao	1	1	1	1
kd	2	2	2	2
Us	0.8	0.8	0.8	0.8
wmax	1	1	0.8	0.8
fb	0	1	-5.148e-18	1
a	0	1	0	1
P	-8	142	-8	142
ra	-0	-0	-5	-5

We find $U = 0.8$ to maximize the profit. $X = 1$ and $a = 0$ exiting the reactor.

P10-19

a) Start with the mole balance for a batch reactor:

$$\frac{dX}{dt} = \frac{-r'_T W}{N_{T0}}$$

Rate law:

$$-r'_T = k_7 P_7 a$$

Decay law:

$$-\frac{da}{dt} = k_d a^2$$

Stoichiometry:

$$P_7 = P_{T0}(1 - X)$$

Plugging those into POLYMATH gets the following program and the following graph

Equations:

$$d(x)/dt = -rt \cdot w / nto$$

$$d(a)/dt = -kd \cdot a^2$$

$$w = 5$$

$$kt = 20$$

$$kd = 1.6$$

$$pto = 1$$

$$v = 1$$

$$R = 0.082$$

$$T = 735$$

$$pt = pto \cdot (1 - x)$$

$$rt = -kt \cdot pt \cdot a$$

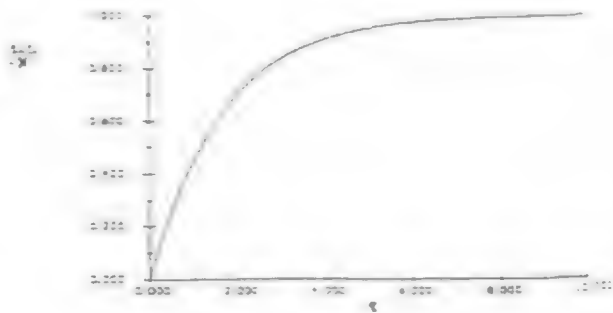
$$nto = pto \cdot v / (R \cdot T)$$

$$t_0 = 0. \quad t_f = 0.001$$

Initial value

0

1



b) For the moving-bed reactor the mole balance now becomes:

$$\frac{dX}{dW} = \frac{-r'_T}{F_{A0}}$$

The decay law now becomes:

$$-\frac{da}{dW} = \frac{k_d a^2}{U_s}$$

P10-19 (cont'd)

Everything stays the same. Plug into POLYMATH.
The conversion achieved is $X = 0.266$

10-19b

Equations:

$$d(x)/d(w) = -rt/f_{ao}$$

$$d(a)/d(w) = -kd \cdot a^2/U_s$$

$$kt = 20$$

$$f_{ao} = 600$$

$$kd = 1.6$$

$$U_s = 2$$

$$pt_o = 2$$

$$pt = pt_o \cdot (1 - x)$$

$$rt = -kt \cdot pt \cdot a$$

$$w_0 = 0, \quad w_f = 50$$

Initial value

0

1

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	50	0	50
x	0	0.26616	0	0.26616
a	1	1	0.0243902	0.0243902
kt	20	20	20	20
fao	600	600	600	600
kd	1.6	1.6	1.6	1.6
Us	2	2	2	2
pto	2	2	2	2
pt	2	2	1.46768	1.46768
rt	-40	-0.715941	-40	-0.715941

c) Increasing U_s will get us a higher conversion. Looking at this summary table, $U_s = 10 \text{ kg/h}$ and $X = 0.6$

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	50	0	50
a	1	1	0.111111	0.111111
x	0	0.599688	0	0.599688
fao	600	600	600	600
kd	1.6	1.6	1.6	1.6
Us	10	10	10	10
kt	20	20	20	20
pto	2	2	2	2
pt	2	2	0.800625	0.800625
rt	-40	-1.77917	-40	-1.77917

(d) For second-order decay:

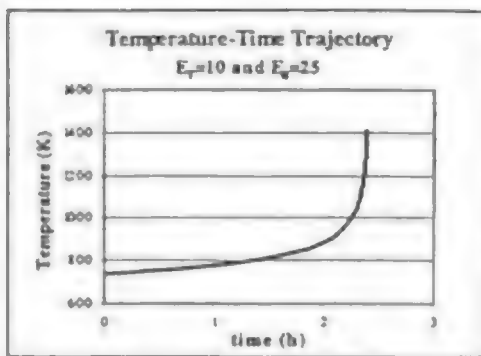
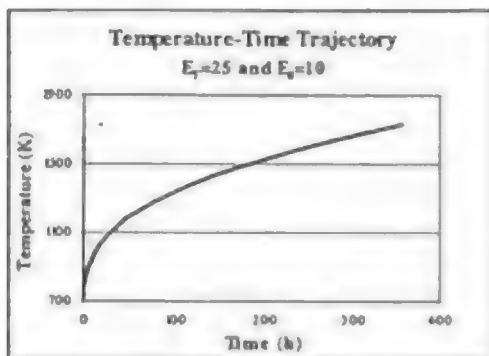
$$t = \frac{1 - \exp\left[\frac{E_T - 2E_d + E_a}{R} \left(\frac{1}{T} - \frac{1}{T_o}\right)\right]}{k_{\infty} (1 - 2 + E_d/E_T)} = \frac{1 - \exp\left[\frac{E_d - E_T}{R} \left(\frac{1}{T} - \frac{1}{T_o}\right)\right]}{k_{\infty} (E_d/E_T - 1)}$$

For $E_T = 25 \text{ kcal/mol}$ and $E_d = 10 \text{ kcal/mol}$:

$$t = \frac{1 - \exp\left[\frac{10 - 25}{0.001987} \left(\frac{1}{T} - \frac{1}{735}\right)\right]}{(1.6)(10/25 - 1)} = -0.96 \left[1 - \exp\left[-7.549 \left(\frac{1}{T} - \frac{1}{735}\right)\right]\right]$$

Use this equation in Excel to generate the following graph:

10-45



For $E_r = 10$ kcal/mol and $E_d = 25$ kcal/mol:

$$t = \frac{1 - \exp\left[\frac{25-10}{0.001987} \left(\frac{1}{T} - \frac{1}{735}\right)\right]}{1.6(25/10-1)} = 2.4 \left[1 - \exp\left[7.549 \left(\frac{1}{T} - \frac{1}{735}\right)\right] \right]$$

Use this equation in Excel to generate the above graph.

(e) In part e, the only thing that changes from (b) is the decay law and the decay constant:

$$-\frac{da}{dW} = \frac{k_d P_T^2 a^2}{U_s}$$

$$k_d = 0.2$$

Plugging into POLYMATH we get the following summary tables for $U_s = 2$ and 10 kg/h. $X = 0.50$ and 0.88 respectively. X will again increase as U_s increases.

Equations:

$$d(x)/d(w) = -ra/fao$$

$$d(a)/d(w) = -kd \cdot pt^2 \cdot a^2 / U_s$$

$$kd = .2$$

$$U_s = 2$$

$$fao = 600$$

$$kt = 20$$

$$pto = 2$$

$$pt = pto \cdot (1-x)$$

$$ra = -kt \cdot pt \cdot a$$

$$w_0 = 0, \quad w_f = 50$$

Initial value

0

1

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	50	0	50
x	0	0.502431	0	0.502431
a	1	1	0.104635	0.104635
kd	0.2	0.2	0.2	0.2
Us	2	2	2	2
fao	600	600	600	600
kt	20	20	20	20
pto	2	2	2	2
pt	2	2	0.995118	0.995118
ra	-40	-2.08253	-40	-2.08253

P10-19 (cont'd)

10-19e

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	50	0	50
x	0	0.875709	0	0.875709
a	1	1	0.553922	0.553922
kd	0.2	0.2	0.2	0.2
Da	10	10	10	10
fao	600	600	600	600
xt	20	20	20	20
pto	2	2	2	2
pt	2	2	0.248581	0.248581
ra	-40	-2.75389	-40	-2.75389

P10-20

(a)

Design Equation: $W = \frac{F_{A0}X}{(-r_A)a(t)} \Rightarrow a(t) = \frac{v_0}{W} \left(\frac{C_{A0} - C_A}{kC_A^n} \right)$ For n^{th} order kinetics

Assume at $t = 0$, $a(0) = 1$ and $X = 1$.

$$\Rightarrow F_B(0) = F_{A0}X = F_{A0} = 106 \Rightarrow F_{A0} = 106$$

Now

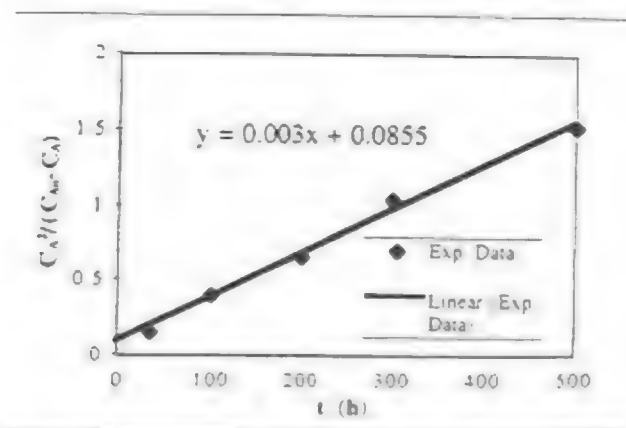
$$F_B(t) = F_{A0}X(t) = \text{RON}(t)$$

$$X(t) = \frac{\text{RON}(t)}{106} = \frac{\text{RON}(t)}{\text{RON}(0)}$$

Second order kinetics and second order decay rate fit the data very well.

$$a'(t) = -k_d a^2 \Rightarrow a(t) = \frac{1}{1 + k_d t} \Rightarrow 1 + k_d t = \frac{kC_A^2}{C_{A0} - C_A}$$

Plot of $\frac{C_A^2}{C_{A0} - C_A}$ vs. t :



10-47

P10-20 (cont'd)

From the graph : intercept = $1/k = 0.0835 \Rightarrow k = 11.98$
 slope = $k_d/k = 0.003 \Rightarrow k_d = 0.00025$

- (b) Activation Energies both for rate constant and decay constant can be estimated from the temperature-time trajectory.

P10-21

a) In order to get a high conversion the entering pressure should be as high as possible since the rate is a second order function of the pressure. U should be kept low since the conversion is an indirect function of the flow rate.

b) The problem with such a low flow rate is that the activity will remain low.

c) We can use the same equations that are given in example 10-7 with a few exceptions. For example the rate law, we use the one given in the problem:

$$-r'_a = k P_A^2$$

The activity will be different because the equation given is different:

$$-\frac{da}{dt} = k_D a C_{\text{coke}}$$

$$-\frac{da}{dz} = \frac{k_D a C_{\text{coke}}}{U}$$

To find the concentration of coke we use stoichiometry:

$$P_{\text{coke}} = P_{A0} \frac{X}{1 + \epsilon X}$$

$$C_{\text{coke}} = \frac{P_{\text{coke}}}{RT}$$

We find that the value that gives the best conversion ($X = 0.337$) and uses the whole reactor is $U = 7$. See the following POLYMATH program.

10-48

P10-21 (cont'd)

Equations:

$$d(a)/d(z) = -k_d \cdot a \cdot c_{\text{coke}}/U$$

$$d(x)/d(z) = -r_a/U/c_{\text{ao}}$$

$$c_{\text{ao}} = .22$$

$$k_d = 100$$

$$k_{\text{prime}} = 5e-5$$

$$U_0 = 7$$

$$\epsilon = 1$$

$$R = .082$$

$$T = 673$$

$$p_{\text{ao}} = 12$$

$$\rho = 80$$

$$U = U_0 \cdot (1 + \epsilon \cdot x)$$

$$p_a = p_{\text{ao}} \cdot (1 - x) / (1 + \epsilon \cdot x)$$

$$p_{\text{coke}} = p_{\text{ao}} \cdot x / (1 + \epsilon \cdot x)$$

$$r_{\text{apime}} = a \cdot (-k_{\text{prime}} \cdot p_a^2)$$

$$c_{\text{coke}} = p_{\text{coke}}/R/T$$

$$r_a = \rho \cdot r_{\text{apime}}$$

$$z_0 = 0, \quad z_f = 15$$

Initial value

1

0

Variable	Initial value	Maximum value	Minimum value	Final value
z	0	15	0	15
a	1	1	0.000254948	0.000254948
x	0	0.136731	0	0.136731
c _{ao}	0.22	0.22	0.22	0.22
k _d	100	100	100	100
k _{prime}	5e-05	5e-05	5e-05	5e-05
U ₀	7	7	7	7
ε	1	1	1	1
R	0.082	0.082	0.082	0.082
T	673	673	673	673
p _{ao}	12	12	12	12
ρ	80	80	80	80
U	7	9.35712	7	9.35712
p _a	12	12	5.95425	5.95425
p _{coke}	0	1.02288	0	1.02288
r _{apime}	-0.0072	-4.51934e-07	-0.0072	-4.51934e-07
c _{coke}	0	0.0547762	0	0.0547762
r _a	-0.576	-3.61547e-05	-0.576	-3.61547e-05

d) To find this the only change necessary was the values for the k's because they change with temperature.

$$k_R = 5 \times 10^{-5} \exp \left[\frac{E_R}{R} \left(\frac{1}{673} - \frac{1}{T} \right) \right]$$

$$k_D = 100 \exp \left[\frac{E_D}{R} \left(\frac{1}{673} - \frac{1}{T} \right) \right]$$

The POLYMATH program below shows the results. The temperature is 485K and the conversion is 0.637.

Equations:

$$d(x)/d(z) = -r_a/U/c_{\text{ao}}$$

$$d(a)/d(z) = -k_d \cdot a \cdot c_{\text{coke}}/U$$

$$c_{\text{ao}} = .22$$

$$U_0 = 2.5$$

$$\epsilon = 1$$

$$R = .082$$

$$T = 485$$

$$p_{\text{ao}} = 12$$

$$\rho = 80$$

$$k_d = 100 \cdot \exp(15000/1.987 \cdot (1/673 - 1/T))$$

$$k_{\text{prime}} = 5e-5 \cdot \exp(3000/1.987 \cdot (1/673 - 1/T))$$

$$U = U_0 \cdot (1 + \epsilon \cdot x)$$

$$p_a = p_{\text{ao}} \cdot (1 - x) / (1 + \epsilon \cdot x)$$

$$p_{\text{coke}} = p_{\text{ao}} \cdot x / (1 + \epsilon \cdot x)$$

$$c_{\text{coke}} = p_{\text{coke}}/R/T$$

$$r_{\text{apime}} = a \cdot (-k_{\text{prime}} \cdot p_a^2)$$

$$r_a = \rho \cdot r_{\text{apime}}$$

$$z_0 = 0, \quad z_f = 15$$

Initial value

0

1

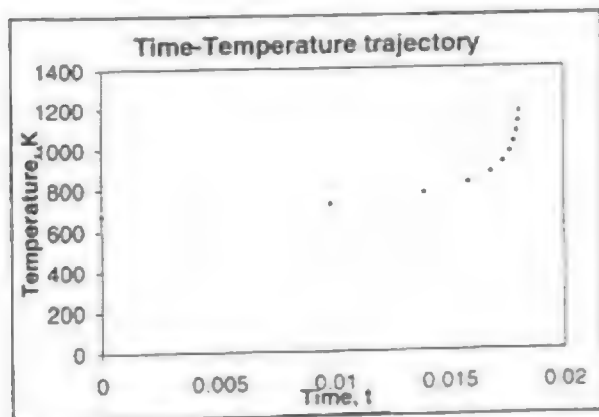
10-49

Variable	Initial value	Maximum value	Minimum value	Final value
z	0	15	0	15
x	0	0.637285	0	0.637285
a	2	1	0.605697	0.605697
cao	0.22	0.22	0.22	0.22
Uo	2.5	2.5	2.5	2.5
eps	1	1	1	1
R	0.082	0.082	0.082	0.082
T	485	485	485	485
pao	12	12	12	12
rho	80	80	80	80
kd	1.2932	1.2932	1.2932	1.2932
kprime	2.09558e-05	2.09558e-05	2.09558e-05	2.09558e-05
U	2.5	4.09321	2.5	4.09321
pa	12	12	2.65841	2.65841
pcoke	0	4.6708	0	4.6708
ccoke	0	0.117445	0	0.117445
reprime	-0.00301763	-0.97021e-05	-0.00301763	-0.97021e-05
ra	-0.24141	-0.00717616	-0.24141	-0.00717616

e) To find the temperature-time trajectory, use equation (10-119) and add C_{coke} where necessary:

$$t = \frac{1 - \exp \left[\frac{E_A - nE_A + E_d}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]}{k_{d0} (1 - n + E_d/E_A) C_{\text{coke}}}$$

The following curve is generated from that equation.

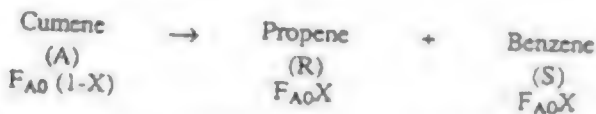


P10-22



Design equation: $r = \frac{F_{A0}X}{W}$

Assume $W = 1g \therefore r = F_{A0}X$



The amount of cumene hydroperoxide does not contribute significantly to the total number of moles.

$$y_S = \frac{F_{A0}X}{F_{A0}(1-X) + F_{A0}X + F_{A0}X} = \frac{X}{1+X} \quad \text{or} \quad X = \frac{y_S}{1-y_S}$$

$$\therefore r = F_{A0} \left(\frac{y_S}{1-y_S} \right)$$

$$a = \frac{r}{r_0} = \frac{\left(\frac{y_S}{1-y_S} \right)}{\left(\frac{y_S}{1-y_S} \right)_{h=0}}$$

X	0.204	.0165	.0133	.0107	.00857	.00563	.00371	.00241
a	1	.809	.652	.5245	.420	.276	.182	.118
t	0	50	100	150	200	300	400	500

In a vs. t gives the best fit $a = e^{-\alpha t}$

$$\alpha = 4.27 \times 10^{-3} \text{ (sec}^{-1}\text{)}$$

Therefore, decay is first order with decay constant of $4.27 \times 10^{-3} \text{ (sec}^{-1}\text{)}$

(b) $C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v}$

Assume no ΔP : $\frac{v}{v_0} = \frac{n}{n_0} = \frac{F_{A0}(1+X)}{F_{A0}} \Rightarrow v = (1+X)v_0$

$$C_A = \frac{F_{A0}(1-X)}{v_0(1+X)} = C_{A0} \frac{(1-X)}{(1+X)}$$

$$P_A = C_A RT = C_{A0} \frac{(1-X)}{(1+X)} RT$$

Mass balance : $F_{A0} dX = r dW$

$$r = e^{-\alpha t} k P_A$$

$$t = \frac{W}{U_S}$$

P10-22 (cont'd)

$$\therefore F_{A0} dX = e^{-\left(\frac{\alpha W}{U_s}\right)} k P_A dW$$

$$\text{or } \frac{F_{A0}}{C_{A0} RT} \int_0^X \frac{1+X}{1-X} dX = k \int_0^W e^{-\left(\frac{\alpha W}{U_s}\right)} dW \quad (1)$$

$$F_{A0} = 20 \text{ mol/min} = 1/3 \text{ mol/sec}$$

$$C_{A0} = 0.06 \text{ kmol/m}^3 = 0.06 \text{ mol/l}$$

$$R = 0.082 \frac{\text{atm} \cdot \text{l}}{\text{K} \cdot \text{mol}}$$

$$T = 273 + 420 = 693 \text{ K}$$

$$k = 3.8 \times 10^{-3} \text{ mol/g sec atm}$$

$$\alpha = 4.27 \times 10^{-3} \text{ sec}^{-1}$$

$$W = 100 \text{ kg}$$

$$U_s = 10 \text{ kg/min} = 1/6 \text{ kg/sec}$$

Equation (1) becomes:

$$2 \ln(1-X) + X = \frac{C_{A0} RT k U_s}{F_{A0} \alpha} \left[e^{-\left(\frac{\alpha W}{U_s}\right)} - 1 \right]$$

$$2 \ln(1-X) + X = \frac{(0.06)(0.082)(693)(3.8 \times 10^{-3}) \left(\frac{1000}{6}\right)}{\left(\frac{1}{3}\right)(4.27 \times 10^{-3})} \left[\exp \left\{ -\frac{4.27 \times 10^{-3} \times 1000}{\frac{1}{6}} \right\} - 1 \right]$$

$$= -1.4 \times 10^3$$

$$\therefore X \cong 1.00$$

P10-23

Given $A \rightarrow R + S$

Batch constant volume reactor, P increases with time

$$N_{A0} dX = a r_0 W dt$$

Assume $a = e^{-\alpha P}$

$$r_0 = k P_A$$

$$\therefore P_A = C_A RT$$

$$C_A = \frac{N_{A0}(1-X)}{V} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X)$$

$$\therefore N_{A0} dX = W e^{-\alpha P} k C_{A0}(1-X) RT dt$$

10-52

$$\int_0^x \frac{dX}{1-X} = \frac{W k C_{A0} RT}{N_{A0}} \int_0^t e^{-\alpha t} dt = \left(\frac{W}{V_0}\right) k RT \int_0^t e^{-\alpha t} dt$$

$$= \beta \int_0^t e^{-\alpha t} dt \quad \text{where } \beta = \left(\frac{W}{V_0}\right) k RT$$

$$-\ln(1-X) = \frac{\beta}{\alpha} (1 - e^{-\alpha t})$$

Assume that there is very little deactivation in the first 10 sec

$$-\ln(1-X) = \frac{\beta}{\alpha} (\alpha t) = \beta t \quad (\text{for small } t)$$

$$\beta = \frac{1}{t} \ln\left(\frac{1}{1-X}\right) = \frac{1}{10} \ln\left(\frac{1}{1-0.037}\right) = 3.77 \times 10^{-3} \text{ sec}$$

$$\beta = \left(\frac{W}{V_0}\right) k RT \Rightarrow k = \frac{\beta}{\left(\frac{W}{V_0}\right) RT} = \frac{3.77 \times 10^{-3}}{1 \times 0.08205 \times (273+420)}$$

$$k = 6.63 \times 10^{-5} \text{ sec}^{-1}$$

At t relatively large, $e^{-\alpha t} = 0$

$$\frac{\beta}{\alpha} = -\ln(1-X)$$

$$\alpha = \frac{\beta}{\ln\left(\frac{1}{1-X}\right)} = \frac{3.37 \times 10^{-3}}{\ln\left(\frac{1}{1-0.517}\right)} = 5.18 \times 10^{-3} \text{ sec}^{-1}$$

$$\therefore -\ln(1-X) = 0.728 (1 - e^{-5.18 \times 10^{-3} t})$$

t	X	X
0	0	0
10	0.037	0.036
20	0.071	0.069
30	0.102	0.099
40	0.130	0.127
60	0.180	0.177
80	0.223	0.219
100	0.259	0.255
150	0.330	0.325
200	0.379	0.375
300	0.441	0.437
500	0.493	0.490
750	0.512	0.510
1000	0.517	0.515

∴ The assumption of a first order reaction kinetics and a first order decay kinetics is justified.

cyclopentane < n-pentane
coke

Batch mole balance : $-\frac{dN_A}{dt} = -r_A W = k_A C_A^* W$
 $-\frac{dC_A}{dt} = \frac{k_A}{V} C_A^* W$
 $-\frac{da}{dt} = k_A a^* C_A^* = k_A a^*$, with C_A constant

Assume $q = 2$: $a = \frac{1}{1 + k_d t}$

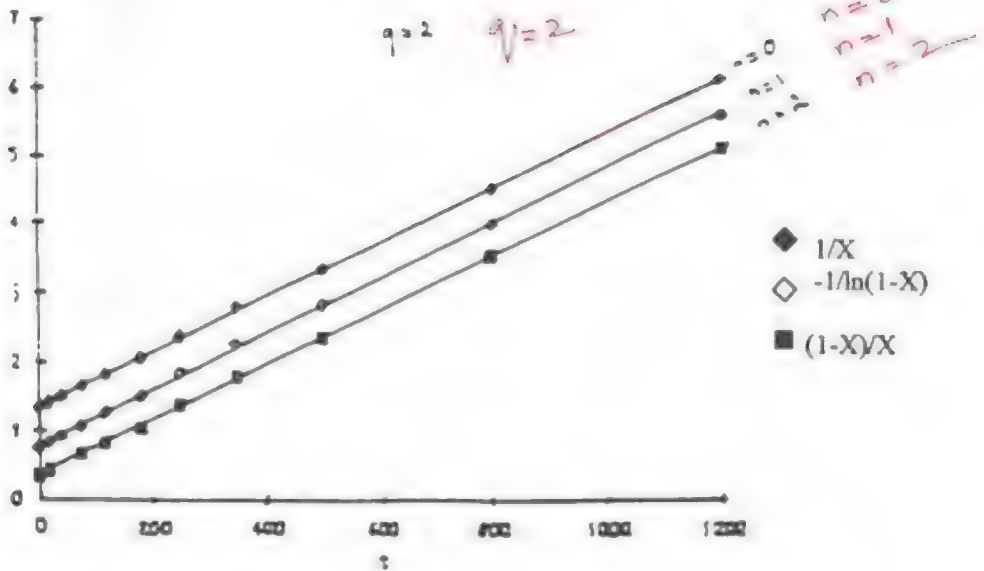
If $n = 0$: $\frac{1}{X} = \frac{1}{k\tau} + \frac{k_d}{k\tau} t$

If $n = 1$: $\frac{1}{-\ln(1-X)} = \frac{1}{k\tau} + \frac{k_d}{k\tau} t$

If $n = 2$: $\frac{(1-X)}{X} = \frac{1}{k\tau} + \frac{k_d}{k\tau} t$

t	X(%)	$\frac{1}{X}$	$\frac{1}{-\ln(1-X)}$	$\frac{(1-X)}{X}$
0	75	1.33	0.721	0.333
20	70.7	1.414	0.815	0.415
40	67	1.493	0.902	0.493
80	60.5	1.653	1.076	0.653
120	55.2	1.811	1.245	0.817
180	48.7	2.053	1.498	1.053
250	42	2.381	1.836	1.381
350	36	2.778	2.241	1.777
500	30	3.333	2.804	2.333
800	22	4.545	4.025	3.545
1200	16.3	6.135	5.620	5.135

P10-24 (cont'd)



From the above graph, all lines are straight lines. Therefore, $q = 2$ is a good assumption.

We need to examine the data to see which value of n having $\frac{\Delta y}{\Delta t} = \text{constant}$. $n = 0$ and $n = 2$ will have similar behavior of $\frac{\Delta y}{\Delta t}$ because:

$$\frac{1-X}{X} = \frac{1}{X} - 1$$

$$n = 1: \Delta y = \Delta \left[\frac{1}{-\ln(1-X)} \right] \text{ and } \Delta t = 20 \text{ min}$$

$$\frac{\Delta y}{\Delta t} = 0.094; 0.087; 0.087; 0.084; \dots; 0.081; \dots; 0.0797$$

Therefore, $\frac{\Delta y}{\Delta t}$ is decreasing gradually. It is not a constant.

$$\text{For } n = 0, n = 2: \frac{\Delta y}{\Delta t} = 4 \times 10^{-3} = \text{constant}$$

$$\text{If } n = 0: -\frac{dC_A}{dt} = K_R \left(\frac{1}{1 + k_d t} \right)$$

$$\frac{dX}{dt} = \frac{K_R}{C_{A0}} \left(\frac{1}{1 + k_d t} \right)$$

$$\frac{dt}{dX} = \frac{C_{A0}}{K_R} + \frac{C_{A0} k_d}{K_R} t$$

10-55

P10-24 (cont'd)

$$\text{If } n=2: -\frac{dC_A}{dt} = K_R \left(\frac{1}{1 + k_d t} \right) C_A^2$$

$$\frac{1}{(1-X)^2} \frac{dX}{dt} = \frac{K_R C_{A0}}{1 + k_d t}$$

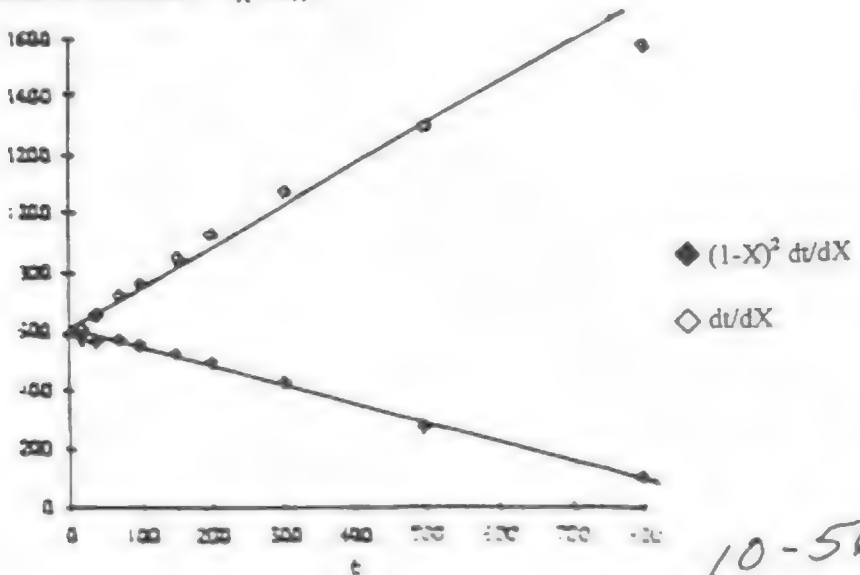
$$(1-X)^2 \frac{dt}{dX} = \frac{1}{K_R C_{A0}} + \frac{k_d}{K_R C_{A0}} t$$

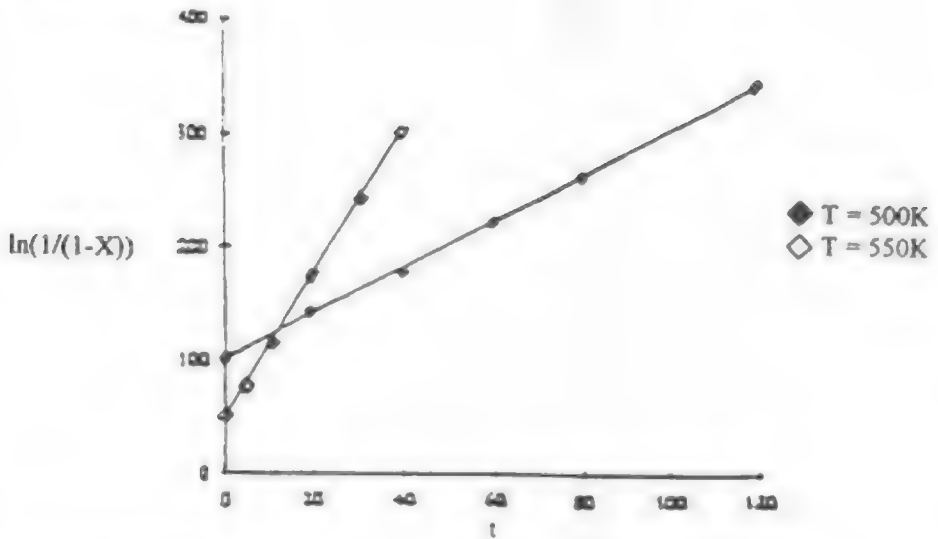
t	X%	$\frac{\Delta X}{\Delta t}$	$\frac{\Delta t}{\Delta X}$	$\frac{dt}{dX}$	$(1-X)^2 \frac{dt}{dX}$
0	0	1.7×10^{-3}	588	587	587
10	1.7	1.7×10^{-3}	588	600	579
20	3.4	1.6×10^{-3}	625	610	569
40	6.6	1.47×10^{-3}	680	650	567
70	11	1.33×10^{-3}	752	720	570
100	15	1.3×10^{-3}	769	760	549
150	21.5	1.14×10^{-3}	877	850	524
200	27.2	9.9×10^{-4}	1010	930	492
300	37.1	8.4×10^{-4}	1190	1075	425
500	53.9	6.9×10^{-4}	1449	1300	276
800	74.6	3.43×10^{-4}	2919	1580	102
1200	88.3				

$n=2$: Slope is negative. It is unreasonable

$n=0$: $\frac{dt}{dX}$ vs. t is a straight line.

The reaction is zero-order: $-r_A = k_A a$





They are straight lines $\therefore n=2$

$$\left. \begin{array}{l} \text{For } T_1 = 500 \text{ K : slope} = 2.04 \frac{K_d}{(\tau K)_1} \\ \text{[Intercept]} = 0.01 = (\tau K)_1 \end{array} \right\} \Rightarrow K_{d1} = 0.02$$

$$\left. \begin{array}{l} \text{For } T_2 = 550 \text{ K : slope} = 6.325 \\ (\tau K)_2 = 0.02 \end{array} \right\} \Rightarrow K_{d2} = 0.1265$$

$$\frac{K_{d1}}{K_{d2}} = \frac{0.02}{0.1265} = \exp \left\{ \frac{E_d}{8.314} \left(\frac{1}{550} - \frac{1}{500} \right) \right\}$$

$$E_d = 84,344 \frac{\text{J}}{\text{mol}}$$

$$K_{d1} = K_{d2} \exp \left\{ -\frac{E_d}{R} \left(\frac{1}{T_1} \right) \right\} = K_{d2} \exp \left\{ -\frac{84,344}{8.314} \left(\frac{1}{500} \right) \right\} = 0.02$$

$$K_{d1} = 1.296 \times 10^{-3}$$

We want to maintain $K_d = \text{constant}$

$$K \left(\frac{1}{1 + K_d t} \right) = K_0$$

$$K_0 \exp \left\{ \frac{E}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right\} = K_0 (1 + K_d t)$$

$$\exp \left\{ \frac{E}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right\} - 1 = K_d t$$

$$t = \frac{\exp \left\{ \frac{E}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right\} - 1}{K_d}$$

P10-24 (cont'd)

$$C_{A0} = 0.03 \frac{\text{kmol}}{\text{m}^3}$$

$$W = 0.01 \text{ kg/m}^3$$

$$\tau = \frac{C_{A0}W}{F_{A0}} = \frac{\left(0.03 \frac{\text{kmol}}{\text{m}^3}\right) \left(0.01 \frac{\text{kg}}{\text{m}^3}\right)}{1.5 \times 10^{-5} \text{ kmol/min}} = 20 \frac{\text{kg}}{(\text{m}^3)^2} \text{ min}$$

(b) The order of decay is $q=2$

$$\frac{k_d}{k_A} = 4 \times 10^{-3} \Rightarrow k_d = 3 \times 10^{-3} \text{ min}^{-1}$$

(c) Moving bed reactor: $F_{A0} = \frac{2 \text{ kmol}}{\text{min}}$; $X = 0.80$

$$-\frac{da}{dt} = k_d a^2 \quad (1)$$

$$F_{A0} \frac{dX}{dW} = -r_A = k_A a \quad (2)$$

In moving bed: $t = \frac{W}{u}$ where $u = \frac{\text{mass}}{\text{time}}$

$$dt = \frac{1}{u} dW$$

Substitute into equation (1): $-\frac{da}{dW} = \frac{k_d}{u} a^2$

$$-\frac{da}{a^2} = \frac{k_d}{u} dW$$

$$1 - \frac{1}{a} = \frac{k_d}{u} W$$

$$a = \frac{1}{1 + \frac{k_d W}{u}}$$

Substitute into equation (2), we have:

$$F_{A0} \int_0^X \frac{dX}{k_A a} = F_{A0} \int_0^X \frac{dX}{k_A \left(\frac{1}{1 + \frac{k_d W}{u}} \right)} = \int_0^W dW$$

$$\frac{F_{A0}}{k_A} \int_0^X dX = \int_0^W \frac{dW}{1 + \frac{k_d W}{u}}$$

$$\frac{F_{A0}}{k_A} X = \frac{u}{k_d} \ln \left(1 + \frac{k_d W}{u} \right)$$

$$\frac{u}{k_d} \ln \left[1 + \frac{k_d W}{u} \right]$$

$$W = \frac{u}{k_d} \left[\exp \left(X \frac{F_{A0} k_d}{u k_A} \right) - 1 \right]$$

10-58

P10-24 (cont'd)

$$W = \frac{u}{3 \times 10^{-3}} \left\{ \exp \left(\frac{0.8 \times 2 \times 3 \times 10^{-3}}{0.0375 \times} \right) - 1 \right\}$$

If $u = 1 \frac{\text{kg}}{\text{min}}$ $W = 45.5 \text{ kg}$

(d) If $u = 0.5 \frac{\text{kg}}{\text{min}}$ $W = 48.6 \text{ kg}$

P10-25

a) $S \rightarrow W + \text{CO}_2$: first order, irreversible.

$$- \frac{da}{dt} = k_d a^n C_A^m = k_d a^n$$

$$-r_A = K_d C_A$$

Assume $n=2$: $a = \frac{1}{1 + k_d t}$

$$\ln \left(\frac{1}{1-X} \right) = \frac{\tau K}{1 + K_d t}$$

$$\frac{1}{\ln \left(\frac{1}{1-X} \right)} = \frac{1}{\tau K} + \frac{K_d}{\tau K} t$$

For $T = 500 \text{ K}$

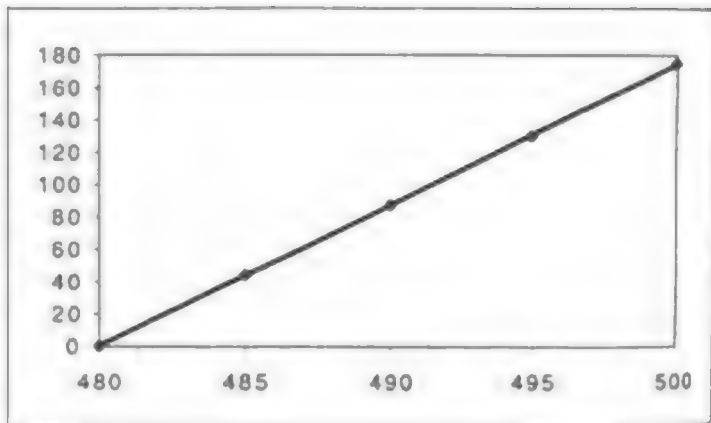
$t(\text{min})$	0	20	40	60	80	120
$X\%$	1	0.7	0.56	0.45	0.38	0.29
$1/\ln \left(\frac{1}{1-X} \right)$	99.5	142.4	178.1	221.7	262.6	344.3

For $T = 550 \text{ K}$

$t(\text{min})$	0	5	10	15	20	30	40
$X\%$	2	1.2	0.89	0.69	0.57	0.42	0.33
$1/\ln \left(\frac{1}{1-X} \right)$	49.5	82.8	111.8	144.4	174.9	237.6	302.5

$$\tau = \frac{\exp\left\{\frac{150,000}{8,314}\left(\frac{1}{480} - \frac{1}{T}\right)\right\} - 1}{1.296 \times 10^7 \exp\left\{-\frac{84,344}{8,314 T}\right\}}$$

T(°K)	t(min)
480	0
485	44.3
490	87.3
495	130.4
500	174.9

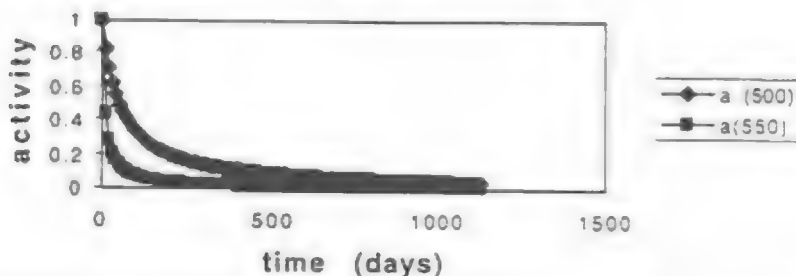


b) Since the equation for the activation is:

$$a = \frac{1}{1 + k_d t}$$

we cannot find a time for which $a = 0$, because it is mathematically impossible. We can, however, find a time at which the activity is small enough that it can be considered to be zero. The following graphs show the activation for the two temperatures given.

Activity of catalyst



The graphs show that for 500 K, the lifetime is about 1100 days and for 550 K, the lifetime is about 450 days.

P10-26

First we need to find C_{A0} .

$$\frac{H_s}{ETB} = 10$$

$$y_{ETB} = 0.1$$

$$C_{A0} = \frac{P y_{ETB}}{RT} = \frac{3 \cdot 10^3 (0.1)}{(8309)553} = 0.065$$

Start by guessing that the decay is first order.

$$k_d t = \ln(k_d) + \ln \frac{C_A}{C_{A0} - C_A}$$

We were told that the reaction is zero-order when the conversion is less than 0.75. This is true at any time after 2 hours. We also need to find the denominator as a function of conversion.

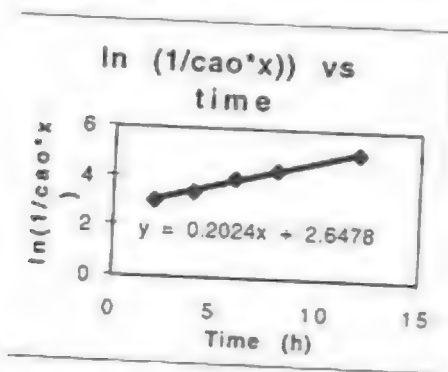
$$X = \frac{C_{A0} - C_A}{C_{A0}}$$

$$C_{A0} - C_A = C_{A0} X$$

So we graph this:

$$\ln \frac{1}{C_{A0} X} \text{ vs. } t$$

This is the graph that we get:



As can be seen this graph is linear which means that the decay is first order. We also know that the slope will be the decay law constant so $k_d = 0.2024$.

P10-27

a) Mass balance:

$$\frac{dX}{dW} = \frac{-r_A}{F_{A0}}$$

Rate law:

$$-r_A = k a C_A$$

Decay law:

$$\frac{da}{dW} = \frac{-k_D a}{U_s}$$

Energy balance:

$$\frac{dT}{dW} = \frac{\frac{U_a}{\rho_b} (T_A - T) + (-r_A)(-\Delta H_{R_A})}{U_s C_{ps} + F_{A0} C_{pA}}$$

Stoichiometry

$$C_A = C_{A0} \frac{1-X}{1+\epsilon X}$$

Evaluate the parameters:

$$k = 0.33 \exp \left[3777 \left(\frac{1}{450} - \frac{1}{T} \right) \right]$$

$$k_D = 0.01 \exp \left[7000 \left(\frac{1}{450} - \frac{1}{T} \right) \right]$$

Plug that into POLYMATH and get the following program and answers U_s to get maximum conversion will be 17 kg/s.

P10-27 (cont'd)

10-27

Equations:

$$d(a)/d(w) = -k_d \cdot a / U$$

$$d(x)/d(w) = -r_a / f_{ao}$$

$$d(T)/d(w) = (U_a \cdot (T_a - T) + (-r_a) \cdot (-\Delta H_{rx})) / (U \cdot c_{ps} \cdot f_{ao} \cdot c_{pa})$$

$$f_{ao} = 5.42$$

$$U = 17$$

$$T_a = 323$$

$$\Delta H_{rx} = -80000$$

$$c_{ps} = 100$$

$$c_{pa} = 40$$

$$E_d = 7000$$

$$E_r = 3777$$

$$c_{ao} = .27$$

$$\epsilon_{ps} = 1$$

$$U_a = .8$$

$$k_d = .01 \cdot \exp(E_d \cdot (1/450 - 1/T))$$

$$k_r = .33 \cdot \exp(E_r \cdot (1/450 - 1/T))$$

$$C_a = c_{ao} \cdot (1-x) / (1-\epsilon_{ps} \cdot x)$$

$$r_a = -k \cdot a \cdot C_a$$

$$w_0 = 0, \quad w_f = 50$$

Initial value

1

0

450

10-27

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	50	0	50
a	1	1	0.271596	0.271596
x	0	0.887222	0	0.887222
T	450	645.613	450	645.613
f _{ao}	5.42	5.42	5.42	5.42
U	17	17	17	17
T _a	323	323	323	323
ΔH _{rx}	-80000	-80000	-80000	-80000
c _{ps}	100	100	100	100
c _{pa}	40	40	40	40
E _d	7000	7000	7000	7000
E _r	3777	3777	3777	3777
c _{ao}	0.27	0.27	0.27	0.27
ε _{ps}	1	1	1	1
U _a	0.8	0.8	0.8	0.8
k _d	0.01	1.11401	0.01	1.11401
k	0.33	4.19718	0.33	4.19718
C _a	0.27	0.0161349	0.0161349	0.0161349
-r _a	-0.0891	-0.0161928	-0.14661	-0.0161928

b) Using the same program we can see that the maximum conversion is 0.887.

c) Everything is the same except the energy balance:

$$\frac{dT}{dW} = \frac{U_a w (T_a - T) + h a_p (T_s - T) + (r'_A) (\Delta H_{Rx})}{F_{A0} C_{pA}}$$

We also need an energy balance on the catalyst particles.

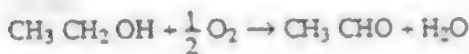
$$\frac{dT_s}{dW} = - \frac{h a_p (T_s - T)}{U_s C_{ps}}$$

Choose values of h and a_p. We find that T_s needs to be slightly higher than T in order to get a large conversion. The maximum conversion will be different for each T_s that is used.

10-63

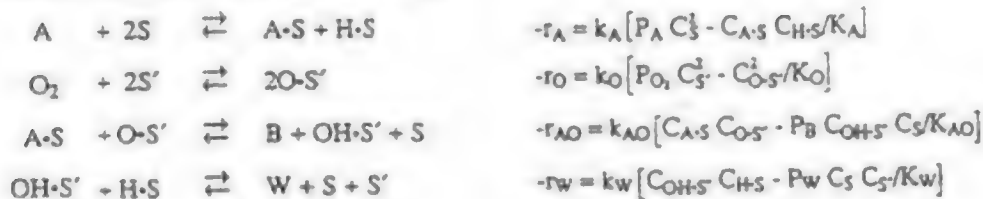
CDP10-A

Given: The catalytic oxidation of ethanol



Denote: A [=] CH₃CH₂OH, B [=] CH₃CHO, W [=] H₂O, A·S [=] CH₃CH₂O·S

Mechanism is believed to be the following:



It is given also that CH₃S = C_{A·S}

With reaction (-r_{AO}) controlling

$$\frac{-r_A}{k_A} \equiv 0 \quad C_{A\cdot S} \text{CH}\cdot\text{S} = K_A P_A C_S^2 \quad \text{or} \quad \text{CH}\cdot\text{S} = C_{A\cdot S} = \sqrt{K_A P_A} C_S$$

$$\frac{-r_{\text{O}}}{k_{\text{O}}} \equiv 0 \quad C_{\text{O}\cdot\text{S}'}^2 = K_{\text{O}} P_{\text{O}_2} C_{\text{S}'}^2 \quad \text{or} \quad C_{\text{O}\cdot\text{S}'} = \sqrt{K_{\text{O}} P_{\text{O}_2}} C_{\text{S}'}$$

$$\frac{-r_W}{k_W} \equiv 0 \quad \text{COH}\cdot\text{S}' \text{CH}\cdot\text{S} = \frac{P_W C_S C_{\text{S}'}}{K_W} \quad \text{with} \quad \text{CH}\cdot\text{S} = \sqrt{K_A P_A} C_S$$

$$\text{COH}\cdot\text{S}' = \frac{P_W C_{\text{S}'}}{K_W \sqrt{K_A P_A}}$$

$$C_T = C_S + \text{CH}\cdot\text{S} + C_{A\cdot S} = C_S [1 + 2\sqrt{K_A P_A}]$$

$$C_T = C_{\text{S}'} + C_{\text{O}\cdot\text{S}'} + \text{COH}\cdot\text{S}' = C_{\text{S}'} \left[1 + \sqrt{K_{\text{O}} P_{\text{O}_2}} + \frac{P_W}{K_W \sqrt{K_A P_A}} \right]$$

$$-r_{\text{AO}} = k_{\text{AO}} \left[C_{A\cdot S} C_{\text{O}\cdot\text{S}'} - \frac{P_B \text{COH}\cdot\text{S}' C_S}{K_{\text{AO}}} \right] = k_{\text{AO}} \left[\sqrt{K_A P_A} K_{\text{O}} P_{\text{O}_2} C_S C_{\text{S}'} - \frac{P_B P_W C_S C_{\text{S}'}}{K_W K_{\text{AO}} \sqrt{K_A P_A}} \right]$$

$$-r_{\text{AO}} = \frac{k_{\text{AO}} \sqrt{K_A K_{\text{O}}} C_S C_{\text{S}'}}{\sqrt{P_A}} \left[P_A \sqrt{P_{\text{O}_2}} - \frac{P_B P_W}{K_A K_W K_{\text{AO}} \sqrt{K_{\text{O}}}} \right]$$

$$K_{\text{eq}} = K_A K_W K_{\text{AO}} \sqrt{K_{\text{O}}}$$

$$-r_{\text{AO}} = \frac{k_{\text{AO}} \sqrt{K_A K_{\text{O}}} C_T C_T \left[P_A \sqrt{P_{\text{O}_2}} - \frac{P_B P_W}{K_{\text{eq}}} \right]}{\sqrt{P_A} [1 + 2\sqrt{K_A P_A}] \left[1 + \sqrt{K_{\text{O}} P_{\text{O}_2}} + \frac{P_W}{K_W \sqrt{K_A P_A}} \right]}$$

CDP10-A (cont'd)

Initially $P_B = P_W = 0$

$$-r_{AO} = \frac{k_{AO} \sqrt{K_A P_A K_O P_{O_2}} C_T C_T}{(1 + \sqrt{K_A P_A})(1 + \sqrt{K_O P_{O_2}})}$$

(b) With reaction 3 irreversible, $-r_{AO} = k_{AO} C_{A \cdot S} C_{O \cdot S}$. Since $A \cdot S$, $H \cdot S$, $OH \cdot S$ are created (and destroyed) only at the reaction surface. A stoichiometric relationship exists between them:

$$C_{H \cdot S} = C_{A \cdot S} + C_{OH \cdot S} \quad (a)$$

The same equilibrium expressions for reactions (1), (2) and (4) exist as before:

$$C_{A \cdot S} C_{H \cdot S} = K_A P_A C_S^2 \quad (b)$$

$$C_{OH \cdot S} C_{H \cdot S} = \frac{P_W C_S C_{S'}}{K_W} \quad (c)$$

$$\therefore (C_{H \cdot S} - C_{A \cdot S}) C_{H \cdot S} = \frac{P_W C_S C_{S'}}{K_W} \Rightarrow C_{H \cdot S}^2 = K_A P_A C_S^2 + \frac{P_W C_S C_{S'}}{K_W}$$

$$\text{or } C_{H \cdot S} = \sqrt{K_A P_A C_S^2 + \frac{P_W C_S C_{S'}}{K_W}}$$

$$C_{A \cdot S} = \frac{K_A P_A C_S^2}{\sqrt{K_A P_A C_S^2 + \frac{P_W C_S C_{S'}}{K_W}}}$$

$$C_{OH \cdot S} = \frac{\frac{P_W C_S C_{S'}}{K_W}}{\sqrt{K_A P_A C_S^2 + \frac{P_W C_S C_{S'}}{K_W}}}$$

Expressions for C_T and C_T' become

$$C_T = C_S + C_{H \cdot S} + C_{A \cdot S} = C_S + \sqrt{K_A P_A C_S^2 + \frac{P_W C_S C_{S'}}{K_W}} + \frac{K_A P_A C_S^2}{\sqrt{K_A P_A C_S^2 + \frac{P_W C_S C_{S'}}{K_W}}}$$

$$C_T' = C_{S'} + \sqrt{K_O P_{O_2}} C_{S'} + \frac{P_W C_S C_{S'}}{\sqrt{K_A P_A C_S^2 + \frac{P_W C_S C_{S'}}{K_W}}}$$

CDP10-A (cont'd)

$$\text{with } K_A P_A C_S^2 \gg \frac{P_W C_S}{K_W}$$

$$C_T = C_S [1 + 2\sqrt{K_A P_A}]$$

$$C_T' = C_S \left[1 + \sqrt{K_O P_{O_2}} + \frac{P_W}{\sqrt{K_A P_A}} \right]$$

Rate expression becomes:

$$-r_A = k_{A0} C_A S C_{O_2} = k_{A0} K_O \sqrt{P_{O_2}} C_S \sqrt{K_A P_A} C_S \left[\frac{1}{\left(1 + \frac{P_W C_S}{K_W K_A P_A C_S} \right)^{1/2}} \right]$$

$$\text{with } \frac{P_W}{\sqrt{K_A P_A}} \ll \sqrt{K_O P_{O_2}}$$

$$-r_A = \frac{k_{A0} K_O \sqrt{P_{O_2}} C_T C_T'}{\left[1 + 2\sqrt{K_A P_A} \right] \left[1 + \sqrt{K_O P_{O_2}} + \frac{P_W}{\sqrt{K_A P_A}} \right]} \left[\frac{1}{\left(1 + \frac{P_W C_S}{K_W K_A P_A C_S} \right)^{1/2}} \right] = \frac{-r_{A0}}{\left(1 + \frac{P_W C_S}{K_W K_A P_A C_S} \right)^{1/2}}$$

$$\frac{C_S}{C_S} = \frac{1}{\mu} \left[\frac{1 + 2\sqrt{K_A P_A}}{1 + \sqrt{K_O P_{O_2}}} \right] \text{ with } \sqrt{K_A P_A} < 1$$

$$-r_A = \frac{-r_{A0}}{1 + \frac{P_W}{\mu K_W K_A P_A} \left[\frac{1}{1 + \sqrt{K_O P_{O_2}}} + \frac{P_W}{\sqrt{K_A P_A}} \right]^{1/2}}$$

CDP10-B

We can first try to come up with a rate law for this data. We can see that as P_E increases the rate law also increases but slowly the amount by which it increases becomes smaller this tells us this:

$$-r_A' \sim \frac{P_E}{1 + K_E P_E}$$

We can then see a similar thing happens as P_H increases so:

$$-r_A' \sim \frac{P_H}{1 + K_H P_H}$$

Since both reactants are adsorbed the mechanism must be a dual site. This makes the rate law:

$$-r_A' = \frac{k P_E P_H}{1 + K_E P_E + K_H P_H}$$

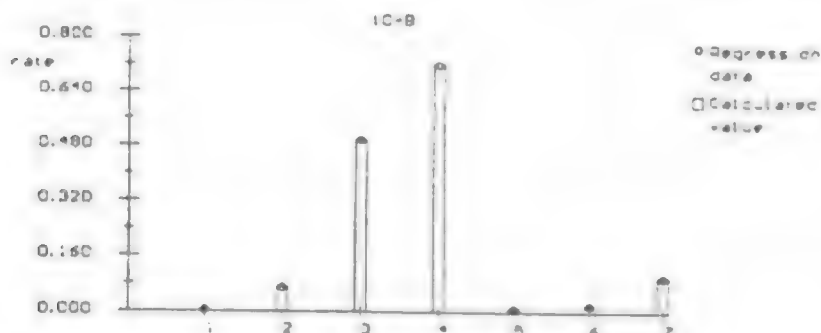
CDP10-B (cont'd)

We can then plug this into POLYMATH and we then get the following values for k , K_E , and K_H .

$$k = 14.6$$

$$K_E = 2.63$$

$$K_H = 1.76$$



Model: $\text{rate} = k \cdot P_{\text{DCS}} \cdot P_{\text{N}_2\text{O}} / (1 + K_E \cdot P_{\text{DCS}} + K_H \cdot P_{\text{N}_2\text{O}})^2$

$$k = 14.5344$$

$$K_H = 1.75782$$

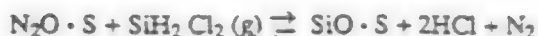
$$K_E = 2.63472$$

3 positive residuals, 6 negative residuals. Sum of squares = 1.45236e-06

CDP10-C



$$r_{\text{SiO}_2} = \frac{k P_{\text{DCS}} P_{\text{N}_2\text{O}}}{(1 + K_{\text{N}_2\text{O}} P_{\text{N}_2\text{O}})^2}$$



$$r_{\text{SiO}_2} = \frac{k P_{\text{DCS}} P_{\text{N}_2\text{O}}}{1 + K P_{\text{N}_2\text{O}}}$$

$$(3) \quad \frac{dF_A}{dV} = r_A' a \quad (\text{Plug Flow Reactor})$$

$$F_{A0} \frac{dX}{dV} = -r_A' a$$

10-67

CDP10-C (cont'd)

$$V = F_{A0} \int_0^X \frac{dX}{-r_A}$$

$$\frac{V_a}{F_{A0}} = \int_0^X \frac{dX}{-r_A}$$

$$-r_A = \frac{k P_{N_2O} P_{DCS}}{1 + K_{N_2O} P_{N_2O}}$$

$$P_{DCS} = P_A = P_{A0} \frac{(1-X)}{(1+\epsilon X)}$$

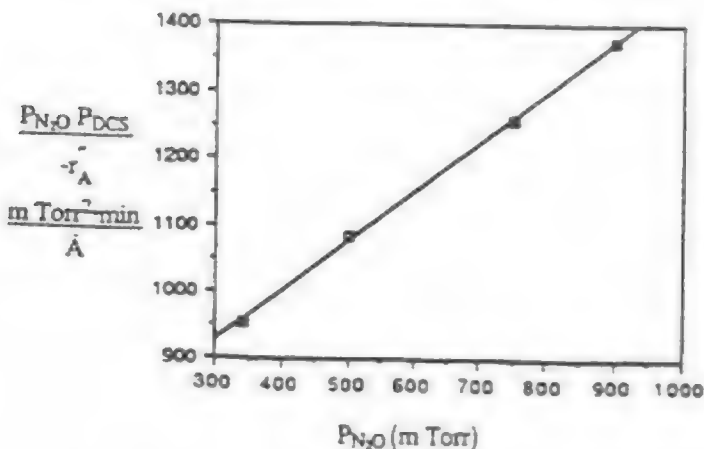
$$P_{N_2O} = P_B = P_{A0} \frac{(\theta_B - 2X)}{(1+\epsilon X)}$$

$$-r_A = \frac{k P_{A0}^2 (1-X)(\theta_B - 2X)}{1 + K_B P_{A0} \frac{(\theta_B - 2X)}{(1+\epsilon X)}}$$

$$= \frac{k P_{A0}^2 (1-X)(\theta_B - 2X)}{(1+\epsilon X)^2 + K_B P_{A0} (\theta_B - 2X)(1+\epsilon X)}$$

$$\theta_B = \frac{11.3}{3.68} = 3.07$$

$$\epsilon = \left(\frac{3.68}{11.3 + 3.68} \right) (2 + 2 \cdot 1 \cdot 2) = 0.25$$



$$\text{Slope} = \frac{K}{k} = 0.7465$$

$$\text{Intercept} = \frac{1}{k} = 703$$

$$k = 1.49 \times 10^{-3} \text{ Å/mTorr}^2 \text{ min}$$

$$K = 1.1 \times 10^{-3} \text{ mTorr}^{-1}$$

$$K_B = 1.1 \times 10^{-3} \text{ m Torr}^{-1} \quad K_B P_{A1} = (1.1 \times 10^{-3})(157) = .173$$

$$k P_{A0}^2 = 1.49 \times 10^{-3} (157)^2 = 36.68 \text{ Å/min}$$

10-68

CDP10-C (cont'd)

$$-r_A = 36.7 \text{ Å/min} \frac{(3.07 - 2X)(1-X)}{(1 + .25X)^2 + .173(3.07 - 2X)(1 + .25X)}$$

$$F_{A0} = 3.68 \times 10^{-3} \text{ gmole/min}$$

$$-r_A = (\text{Å/min}) = 4.4 \times 10^{-6} r_A^* \frac{(\text{gmole})}{(\text{m}^2 \text{ min})}$$

$$a = 250 \text{ m}^2/\text{min}$$

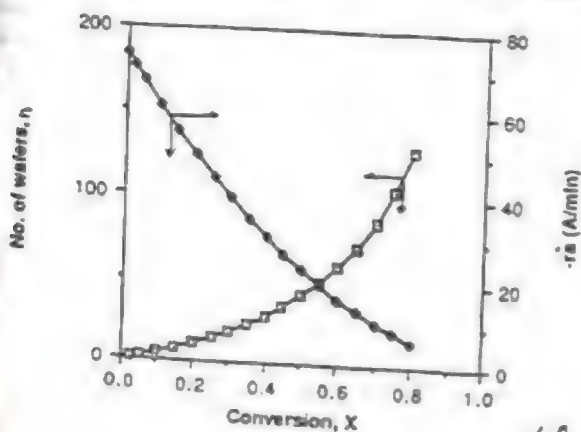
$$\frac{V_A}{F_{A0}} = \int_0^X \frac{dX}{-r_A} \Rightarrow \text{Area under curve of } X \text{ vs. } \frac{1}{-r_A}$$

X	$-r_A^* (\text{Å/min})$	$1/-r_A^* (\frac{\text{min}}{\text{Å}})$	$1/-r_A (\text{m}^2/\text{gmole})$	$\frac{V_A}{F_{A0}}$	V(m ³)
0	73.6	0.0136	3091		0
0.025	70.3	0.0142	3235		0.0012
0.5	67.0	0.0149	3392	79.1	0.0012
0.1	60.8	0.0165	3739	82.8	0.0026
0.15	54.9	0.0182	4139	178.3	0.0029
0.20	49.4	0.020	4545	196.9	0.0032
0.25	44.2	0.0226	5145	217.1	0.0036
0.30	39.3	0.0255	5784	242.3	0.0040
0.35	34.7	0.0288	6547	273.2	0.0045
0.40	30.4	0.0328	7465	308.3	0.0052
0.45	26.5	0.0378	8589	350.3	0.0059
0.50	22.8	0.0439	9983	401.4	0.0068
0.55	19.3	0.0517	11746	464.3	0.0080
0.60	16.2	0.0617	14029	543.2	0.0095
0.65	13.3	0.0751	17067	644.4	0.0114
0.70	10.7	0.0936	21262	777.4	0.0141
0.75	8.3	0.1203	27338	958.2	0.0179
0.80	6.2	0.1617	36760	1215	0.0236

Reactor Volume per wafer = $9.8 \times 10^{-4} \text{ m}^3/\text{wafer}$

∴ Number of wafers, $n = V/9.8 \times 10^{-4}$

A plot of conversion X, vs. number of wafers can be obtained



10-69

CDP10-C (cont'd)

The thickness on these wafers can be obtained from the same plot.

Wafer #1 : $X = 0$

$$-r_A' = 73.6 \text{ Å/min}$$

$$\therefore \text{After 30 min: } \underline{2208 \text{ Å}}$$

Wafer #50 : $X = 0.52$

$$-r_A' = 20 \text{ Å/min}$$

$$\therefore \text{After 30 min: } \underline{600 \text{ Å}}$$

Wafer #110 : $X = 0.78$

$$-r_A' = 6 \text{ Å/min}$$

$$\therefore \text{After 30 min: } \underline{180 \text{ Å}}$$

CDP10-D

a) Mole balance:

$$\frac{dX}{dW} = \frac{-r_A' \cdot a}{F_{A0}}$$

Rate law:

$$r_A' = -kC_A C_B$$

Decay law:

$$\frac{da}{dW} = -\frac{k_d}{U_s} C_B$$

Stoichiometry:

$$C_A = C_{A0}(1 - X)$$

$$C_B = C_{A0}(\theta_B + X)$$

Evaluate the parameters:

$$\theta_B = \frac{C_{B0}}{C_{A0}} = \frac{0.01}{0.1} = 0.1$$

10 - 70

CDP10-D (cont'd)

Equations:

$$d(x)/d(w) = a \cdot (-ra) / fao$$

$$d(a)/d(w) = -kd \cdot cb / U$$

$$kd = 6$$

$$fao = 20$$

$$U = 8$$

$$k = 350$$

$$cao = .1$$

$$\theta_a = .1$$

$$ca = cao \cdot (1 - x)$$

$$cb = cao \cdot (\theta_a + x)$$

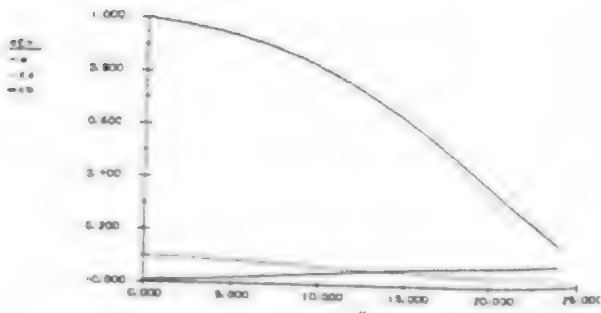
$$ra = -k \cdot ca \cdot cb$$

$$w_0 = 0, \quad w_f = 24$$

Initial value

0

1



b) The only change is in the stoichiometry:

$$C_A = C_{A0}(1 - X)(1 - \alpha W)^{0.5}$$

$$C_B = C_{A0}(\theta_B + X)(1 - \alpha W)^{0.5}$$

POLYMATH

Equations:

$$d(x)/d(w) = a \cdot (-ra) / fao$$

$$d(a)/d(w) = -kd \cdot cb / U$$

$$kd = 6$$

$$fao = 20$$

$$U = 8$$

$$k = 350$$

$$cao = .1$$

$$\theta_a = .1$$

$$\alpha = .038$$

$$ca = cao \cdot (1 - x) \cdot (1 - \alpha w)^{0.5}$$

$$cb = cao \cdot (\theta_a + x) \cdot (1 - \alpha w)^{0.5}$$

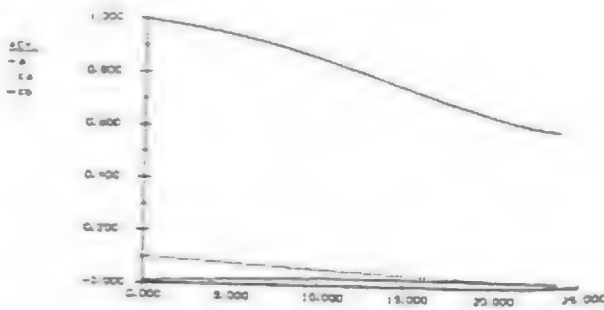
$$ra = -k \cdot ca \cdot cb$$

$$w_0 = 0, \quad w_f = 24$$

Initial value

0

1



CDP10-F

(a) For simplicity, letters were substituted for the species in the problem statement.



The rate equations for each of the three steps in the mechanism is given below.

$$-r_A = k_A \left[P_A P_B^2 - \frac{P_C}{K_A} \right] \xrightarrow{\text{1. adsorption}} P_C = K_A P_A P_B^2$$

$$-r_C = k_C \left[P_C f_v - \frac{f_D}{K_C} \right] \xrightarrow{\text{2. desorption}} f_D = K_C P_C f_v$$

$$-r_{\text{DEP}} = k_S (f_D)(f_v)$$

Equations 1 and 2 are substituted into equation 3 because the third step (the deposition step) is assumed to be the rate limiting step, we want to find the rate law of the deposition, and we have data for the deposition rate.

Also, remember that we have the relation below:

$$f_v + f_D = 1$$

$$f_v = \frac{1}{1 + K_C P_C}$$

Substitute everything into the deposition rate law:

$$-r_{\text{DEP}} = \frac{k_S P_A P_B^2}{(1 + k_2 P_A P_B^2)^2}, \quad \text{where } k_1 \text{ and } k_2 \text{ are constants}$$

We now have to check if the above rate expression agrees with experimental observations.

- The rate of deposition is independent of Ar and H_2 .--YES
- At low partial pressures of TiCl_4 and NH_3 , the deposition appears to be first order in TiCl_4 and second order in NH_3 .--YES

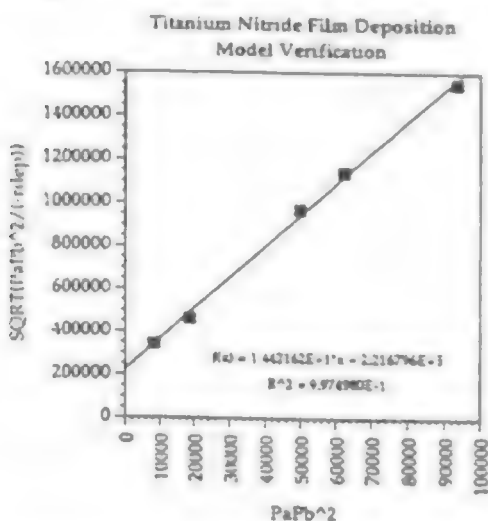
CDP10-F (cont'd)

- At high partial pressures of NH_3 , the rate varies inversely with TiCl_4 .—YES

(b) To determine the reaction rate parameters, we must rearrange the rate expression to a linear form.

$$\sqrt{\frac{P_A P_B^2}{-r_{\text{DEP}}}} = \frac{k_2}{\sqrt{k_1}} P_A P_B^2 + \frac{1}{\sqrt{k_1}}$$

A plot of the experimental data is shown below.



$$\frac{1}{\sqrt{k_1}} = y - \text{intercept} = 2.2168 \times 10^5$$

$$k_1 = 2.035 \times 10^{-11} \frac{\text{mol}}{\text{cm}^2 \cdot \text{min} \cdot \text{mT}^3}$$

$$\frac{k_2}{\sqrt{k_1}} = \text{slope} = 14.42$$

$$k_2 = 6.505 \times 10^{-5} \frac{1}{\text{mT}^3}$$

- (c) The experimental data, when plotted with the rate law derived in this problem, form a straight line. Therefore, the proposed mechanism may be used to describe the deposition of titanium nitride films.

(Solution by J T. Santoro, Jr.)

10-73

CDP10-G (cont'd)

Run 2: $k_d P_A^n = 1.769 \times 10^{-3}$

$P_A = 1$ in run 1 $\Rightarrow k_d = 5.767 \times 10^{-3}$

$P_A = 0.4$ in run 2 $\Rightarrow n = 1.29$

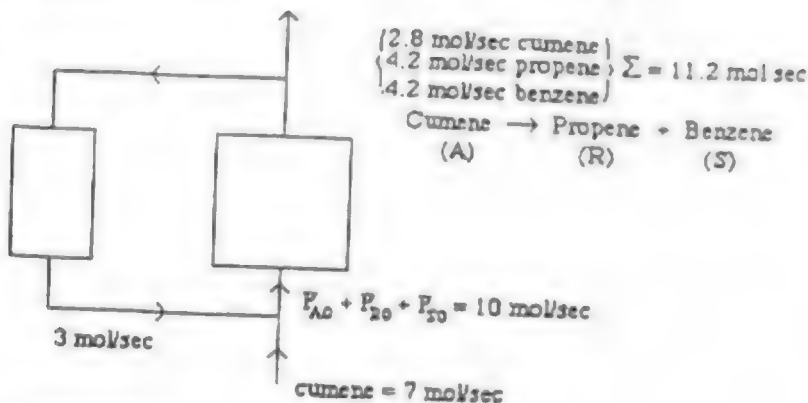
$$r = ar_0 = \frac{k_1 K_A P_A}{1 + k_d P_A^n} \quad k_1 K_A = 3.2 \times 10^{-3}$$

$$k_d = 5.767 \times 10^{-3}$$

$$n = 1.29$$

t in minutes

(c) Overall conversion = 0.60



Composition at reactor outlet

$$y_A = \frac{2.8}{11.2} = 0.25$$

$$y_R = y_S = \frac{4.2}{11.2} = 0.375$$

Composition at reactor inlet, $F_0 = 7 + 3 = 10 \text{ mol/sec}$

$$F_{A0} = 7 + 3(0.25) = 7.75$$

$$y_A = 0.775$$

$$F_{R0} = 3(0.375) = 1.125$$

$$\Rightarrow y_R = 0.1125$$

$$F_{S0} = 3(0.375) = 1.125$$

$$y_S = 0.1125$$

Let $X_f \equiv$ conversion per pass

Total flow at reactor outlet before the recycle stream is:

$$F_{A0}(1-X_f) + 2 F_{A0}X_f + F_{R0} + F_{S0} = F_{A0}(1+X_f) + F_{R0} + F_{S0}$$

$$\therefore y_A = \frac{F_{A0}(1-X_f)}{F_{A0}(1+X_f) + F_{R0} + F_{S0}} = 0.25 \Rightarrow X_f = 0.542$$

10 - 75

CDP10-G (cont'd)

At any point along the reactor:

$$P_A = y_A P_i = y_A \frac{F_{A0}(1-X)}{F_{A0}(1+X) + F_{R0} + F_{S0}} = \frac{1-X}{\beta+X}$$

$$\text{when } \beta = \frac{F_{R0} + F_{S0} + F_{A0}}{F_{A0}} = \frac{10}{7.75} = 1.29$$

Assume that rate law in (b) is still good for the moving bed operation (may not be true in practice because of the high conversion)

$$\therefore r = a k_i K_A P_A = \frac{k_i^* K_A P_A}{1 + k_d P_A^2}$$

$$\text{Moving bed reactor: } t = \frac{W}{U_s}$$

$$F_{A0} dX = -r dW$$

$$\begin{aligned} \frac{dW}{dX} &= \frac{F_{A0}}{-r} = F_{A0} \left[\frac{1 + k_d P_A^2 \frac{W}{U_s}}{k_i^* K_A P_A} \right] = \frac{F_{A0} k_d}{k_i^* K_A U_s} \left(\frac{\beta+X}{1-X} \right)^{n-1} W + \frac{F_{A0}}{k_i^* K_A} \left(\frac{\beta+X}{1-X} \right) \\ &= \frac{7.75 \times 5.767 \times 10^{-3}}{3.2 \times 10^{-3} \times 2000} \left(\frac{1.29+X}{1-X} \right)^{0.29} W + \frac{7.75}{3.2 \times 10^{-3}} \left(\frac{1.29+X}{1-X} \right) \\ &= 6.98 \times 10^{-3} \left(\frac{1.29+X}{1-X} \right)^{0.29} W + 2421 \left(\frac{1.29+X}{1-X} \right) \end{aligned}$$

$$\text{With } X = 0, W = 0$$

$$\text{If } X = 0.542, \text{ using digital computer } W \approx 3.1 \text{ kg}$$

CDP10-H Given: The dehydrogenation of ethyl benzene to styrene:



Quantitative data suggests reaction rate is of the form

$$-r_E \propto \frac{A_1 P_E}{1 + A_2 P_E + A_3 P_{St}} \text{ where } A_1, A_2, A_3 \text{ are constants}$$

The fact that $(-r_E)$ is independent of H_2 suggests that the reaction is irreversible, and that H_2 is not adsorbed on the catalyst surface. Also, the above expression for $(-r_E)$ suggests that both E and St are adsorbed on the surface \therefore Try the following reaction scheme.

10-76

CDP10-H (cont'd)



$$-r_A = k_A [P_E C_S - C_{E \cdot S} / K_A]$$

$$-r_S = k_S [C_{E \cdot S} - C_{St \cdot S} P_{H_2} / K_S]$$

$$-r_D = k_D [C_{St \cdot S} - P_{S_1} C_S / K_D]$$

To insure that P_{H_2} does not appear in the rate expression assume that the surface reaction controls:

$$\frac{-r_A}{k_A} \equiv 0 \quad C_{E \cdot S} = K_A C_S P_E$$

$$\frac{-r_D}{k_D} \equiv 0 \quad C_{St \cdot S} = \frac{C_S P_{S_1}}{K_D}$$

$$\text{Then: } C_T C_S + C_{E \cdot S} + C_{St \cdot S} = C_S \left[1 + K_A P_E + \frac{P_{S_1}}{K_D} \right]$$

$$\text{And } -r_S = k_S \left[C_{E \cdot S} - \frac{C_{St \cdot S} P_{H_2}}{K_S} \right] = k_S K_A C_S \left[P_E - \frac{P_{S_1} P_{H_2}}{K_A K_S K_D} \right]$$

$$\text{or } -r_S = \frac{k_S C_T K_A \left[P_E - \frac{P_{S_1} P_{H_2}}{K_{eq}} \right]}{1 + K_A P_E + \frac{P_{S_1}}{K_D}}, \text{ where } K_{eq} = K_A K_S K_D$$

with $K_S \gg \gg 1$, reaction can be considered irreversible, and its dependence on P_{H_2} drops

$$\text{out: } -r_S = \frac{k K_A P_E}{1 + K_A P_E + \frac{P_{S_1}}{K_D}}, \text{ where } k = k_S C_T$$

Evaluation for k , K_A and K_D

$$\text{Rearranging the rate expression: } \frac{P_E}{-r_S} = \frac{1}{k K_A} + \frac{P_E}{k} + \frac{P_{S_1}}{K_D k K_A}$$

with $P_{S_1} \rightarrow 0$, a plot of $\frac{P_E}{-r_S}$ vs. P_E should be linear with slope $\left(\frac{1}{k}\right)$ and intercept $\left(\frac{1}{k K_A}\right)$. Since only two points are given with $P_{S_1} = 0$, it is easy to solve analytically:

Point	P_E (atm)	$(-r_E)$ gmol/min-gmcat	$P_E / -r_S$
1	1.00	1.415×10^{-3}	706.7
2	0.01	0.214×10^{-3}	46.73

$$\left(\frac{P_E}{-r_S}\right)_1 = \frac{1}{k K_A} + \frac{1}{k} (P_E)_1 \text{ and } \left(\frac{P_E}{-r_S}\right)_2 = \frac{1}{k K_A} + \frac{1}{k} (P_E)_2$$

$$\text{From above: } \frac{1}{k} = \frac{\left(\frac{P_E}{-r_S}\right)_2 - \left(\frac{P_E}{-r_S}\right)_1}{(P_E)_2 - (P_E)_1} = \frac{46.73 - 706.7}{0.01 - 1.0} = 666.7 \frac{\text{gmcat} \cdot \text{min}}{\text{gmole}}$$

$$k = 1.50 \times 10^{-3} \frac{\text{gmol}}{\text{gmcat} \cdot \text{min}}$$

10-77

CDP10-H (cont'd)

$$\text{and } \frac{1}{k K_A} = \left(\frac{P_E}{-r_S} \right)_1 - \frac{1}{k} (P_E)_1 = 706.7 - 666.7 = 40 \frac{\text{atm-gm cat-min}}{\text{gmole}}$$

$$K_A = 16.64 \text{ atm}^{-1}$$

Now, taking data points 1 and 3, in which P_E is constant, the value of K_D & K_A and hence K_D can be determined:

$$\text{For point 1: } \left(\frac{P_E}{-r_S} \right)_1 = \frac{1}{k K_A} + \frac{1}{k} (P_E)_1 + \frac{(P_{S1})_1}{K_D k K_A}$$

$$\text{For point 3: } \left(\frac{P_E}{-r_S} \right)_3 = \frac{1}{k K_A} + \frac{1}{k} (P_E)_3 + \frac{(P_{S1})_3}{K_D k K_A}$$

Subtracting, and solving for $\frac{1}{K_D k K_A}$, noting that $(P_E)_1 = (P_E)_3$

$$\frac{1}{K_D k K_A} = \frac{(P_E)_1 \left[\left(\frac{1}{-r_S} \right)_3 - \left(\frac{1}{-r_S} \right)_1 \right]}{(P_{S1})_3 - (P_{S1})_1} = \frac{1.0 \left[\frac{1}{0.166 \times 10^{-3}} - \frac{1}{1.415 \times 10^{-3}} \right]}{1.0 - 0.0} \frac{\text{gm cat-min}}{\text{gmole}}$$

$$\frac{1}{K_D k K_A} = 5317.3 \frac{\text{gm cat-min}}{\text{gmole}}$$

$$K_D = 0.007534$$

\therefore Rate expression is

$$-r_E = \frac{P_E/40}{1 + 16.64 P_E + \frac{P_{S1}}{0.007534}} = \frac{0.25 P_E}{1 + 16.64 P_E + 132.7 P_{S1}} \left(\frac{\text{gmole}}{\text{gm cat-min}} \right)$$

$$(a) \quad (MW)_E = 106.1 \frac{\text{g}}{\text{gmole}}, \quad (MW)_S = 18 \frac{\text{g}}{\text{gmole}}, \quad (MS)_S = 104.1 \frac{\text{g}}{\text{gmole}}$$

$$\text{Then } \theta_1 = \frac{1 \text{ gmole H}_2\text{O}}{5 \text{ gmole E}} = 0.2$$

$$y_{E0} = \frac{1}{1 + \theta_1} = 0.833 ; \quad P = P_0 = 0.415 ; \quad X_F = 0.60 ; \quad \delta = 2-1 = 1 ; \quad T = 903^\circ\text{K}$$

$$\therefore \varepsilon = y_{E0} \delta = 0.833 ; \quad F_{Sk} = \frac{2000 \text{ Kg}}{\text{day}} \left(\frac{1 \text{ kg mol}}{104.1 \text{ kg}} \right) = 19.2 \frac{\text{kg mol}}{\text{day}} = F_{E0} X_F$$

$$P_E = C_{ERT} = \frac{F_{ERT}}{v} = \frac{F_{E0}(1-X)RT}{v_0(1+\varepsilon X)} = \frac{C_{E0}RT(1-X)}{1+\varepsilon X} = \frac{y_{E0}P_0(1-X)}{1+\varepsilon X}$$

$$P_{S1} = C_{S1}RT = \frac{F_{S1}RT}{v} = \frac{F_{E0} X RT}{v_0(1+\varepsilon X)} = \frac{y_{E0}P_0 X}{1+\varepsilon X}$$

10-78

Rate expression for any X is:

$$-r_E = \frac{0.025 \left[\frac{y_{E,0} P_0 (1-X)}{1+eX} \right]}{1 + 16.64 \left[\frac{y_{E,0} P_0 (1-X)}{1+eX} \right] + \frac{132.7 y_{E,0} P_0 X}{1+eX}}$$

Design expression for a CSTR (fluidized bed) is $W = \frac{F_{E,0} X_F}{-r_E}$

$$W = \frac{F_{E,0} X_F}{0.025 \left[\frac{1+eX_F}{y_{E,0} P_0 (1-X_F)} + 16.64 + \frac{132.7 X_F}{1-X_F} \right]}$$

$$= \frac{F_{St,0} X_F}{0.025 X_F \left[\frac{1+eX_F}{y_{E,0} P_0 (1-X_F)} + 16.64 + \frac{132.7 X_F}{1-X_F} \right]}$$

$$= \frac{19.2 \times 10^3 \text{ gmol}}{\text{day}} \times \frac{1 \text{ day}}{0.025 \left[\frac{1+0.833(0.45)}{0.833(0.415)(1-.45)} + 16.64 + \frac{132.7(0.45)}{1-.45} \right]} \times \frac{1 \text{ day}}{24 \times 60 \text{ min}}$$

$$W = 7.06 \times 10^4 \text{ g}$$

$$\text{Cost} = 70.6 \text{ kg} \times \frac{\$11}{\text{kg}} = \$777$$

(b) Plug flow reactor, expression for $y_{E,0}$, $F_{St,0}$, P_E , P_S , and $-r_E$ are the same as for the CSTR. The design equation is:

$$W = F_{E,0} \int_0^X \frac{dX}{-r_E} = \frac{F_{St,0}}{0.025 X_F} \int_0^X \left[\frac{1+eX}{y_{E,0} P_0 (1-X)} + 16.64 + \frac{132.7 X}{1-X} \right] dX$$

$$W = \frac{F_{St,0}}{0.025 X_F} \left[\frac{1}{y_{E,0} P_0} \{-eX - [1+e] \ln[1-X]\} + 16.64X + 132.7[-X - \ln(1-X)] \right] \Big|_0^X$$

$$W = \frac{F_{St,0}}{0.025 X_F} \left[\frac{1}{y_{E,0} P_0} \{-eX_F - [1+e] \ln[1-X_F]\} + 16.64X_F + 132.7[X_F + \ln(1-X_F)] \right]$$

$$W = \frac{19.2 \times 10^3 \text{ gmol}}{\text{day}} \times \frac{1}{0.025 \times 0.45} \frac{\text{gm cat} \cdot \text{min}}{\text{gmol}}$$

$$\left[\frac{-0.833(0.45) + 1.833 \ln(1-.45)}{(0.833)(0.415)} + 16.64(0.45) + 132.7[0.45 + \ln(1-0.45)] \right] \times \frac{1 \text{ day}}{24 \times 60 \text{ min}}$$

$$W = 2.71 \times 10^4$$

$$\text{Cost} = 27.1 \times \frac{\$11}{\text{kg}} = \$298$$

CDP10-I

a) Mole balance:

$$\frac{dX}{dW} = \frac{a^* - r_A'}{F_{A0}}$$

rate law:

$$-r_A' = k' C_A$$

Stoichiometry:

$$C_A = C_{A0}(1-X)(1-\alpha W)^{0.5}$$

Decay law:

$$-\frac{da}{dW} = \frac{k_d}{U_s} a$$

Evaluate the parameters:

$$\frac{P}{P_0} = (1 - \alpha W)^{0.5}$$

$$\frac{5}{50} = (1 - 100\alpha)^{0.5}$$

$$\alpha = 0.0099$$

$$-\int_1^{0.1} \frac{da}{a} = \frac{k_d}{U_s} \int_0^{100} dW$$

$$\frac{k_d}{U_s} = 0.023$$

POLYMATH

Equations:

$$d(x)/d(w) = -ra^*a/cao$$

$$d(a)/d(w) = -kd^*a$$

$$kd = 0.023$$

$$cao = 4$$

$$k = 0.09$$

$$cao = 2$$

$$alp = 0.0099$$

$$ca = cao^* (1-x)^* (1-alp^*w)^{.5}$$

$$ra = -k^*ca$$

$$w_0 = 0, \quad w_f = 100$$

Initial value

0

1

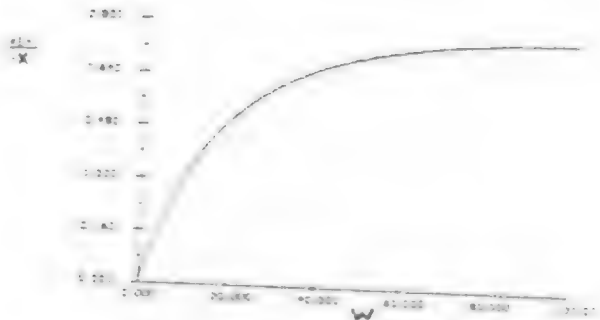
Variable	Initial value	Maximum value	Minimum value	Final value
w	0	100	0	100
x	0	0.757161	0	0.757161
a	1	1	0.100259	0.100259
kd	0.023	0.023	0.023	0.023
cao	4	4	4	4
k	0.09	0.09	0.09	0.09
cao	2	2	2	2
alp	0.0099	0.0099	0.0099	0.0099
ca	2	2	0.0455678	0.0455678
ra	-0.18	-0.0041711	-0.18	-0.0041711

$$X = 0.75$$

10-80

CDP10-I (cont'd)

b) POLYMATH



CDP10-I

Design Equation : $F_{A0} \frac{dX}{dW} = a(W)(1-X)$

Rate Law : $-r'_A = k' C_A$

Decay Law : (for sintering) $a(W) = \frac{1}{1 + k_d \left(\frac{W}{U_s}\right)}$

Stoichiometry : $T = T_0 \Rightarrow C_A = C_{A0}(1-X)$

Combine : $\frac{dX}{dW} = \frac{1}{1 + \frac{k_d}{U_s} W} \frac{k'}{v_0} (1-X) \Rightarrow \frac{dX}{1-X} = \frac{k'}{v_0} \frac{dW}{1 + \frac{k_d}{U_s} W}$

$$\ln\left(\frac{1}{1-X}\right) = \frac{k'}{v_0} \frac{U_s}{k_d} \ln\left(1 + \frac{k_d}{U_s} W\right)$$

From the problem statement, $a_{\text{ext}} = \frac{1}{1 + \frac{k_d}{U_s} W} = \frac{1}{4}$

Plugging in 100 kg for W, we can solve for $\frac{k_d}{U_s}$.

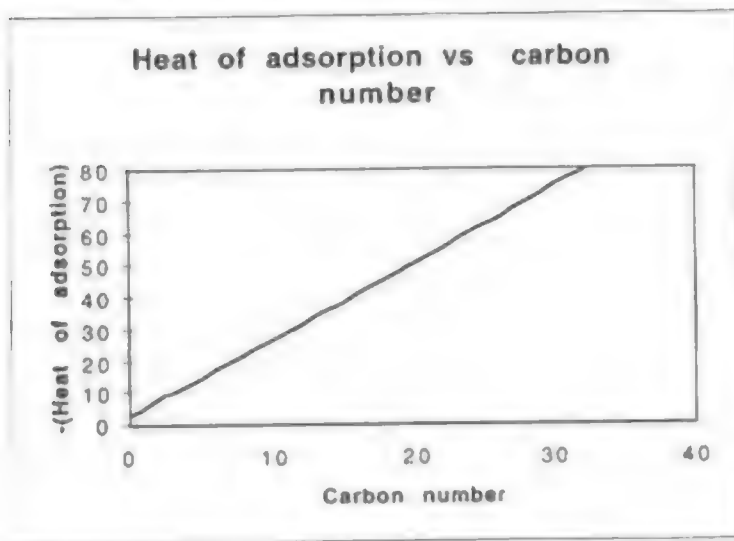
$$\frac{k_d}{U_s} = 0.03$$

$$\ln\left(\frac{1}{1-X}\right) = \frac{(0.10)}{(3.75)(0.03)} \ln(1 + (0.03)(100)) = 1.232 \Rightarrow \frac{1}{1-X} = 3.43$$

$$X = 0.708$$

10-81

The heat of activation is given in the problem as a function of the carbon number so we can just graph that:



To graph the activation energy we need to find its equation. It is the Arrhenius equation.

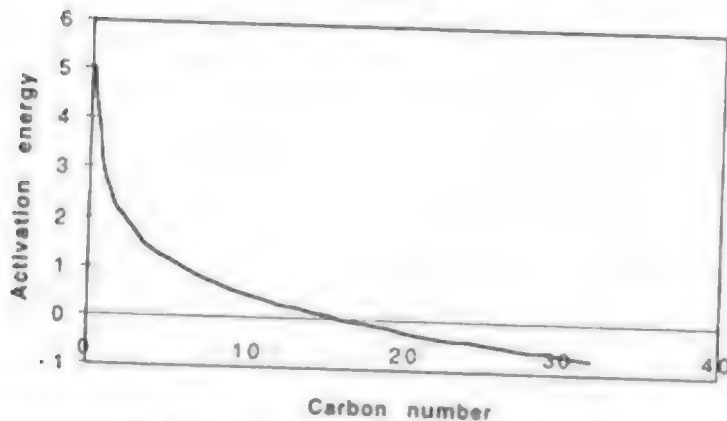
$$k = Ae^{-E/RT}$$

Solving for E we get:

$$E = -RT \ln\left(\frac{k}{A}\right)$$

We know that as the temperature increases when $n \leq 15$, the rate increases so k still gets larger with greater temperature so E is still positive. When the temperature increases when $n > 15$, the rate decreases so k decreases making E negative. So we can come up with some equation with the above equation that fits this criteria and we can come up with the following graph.

Activation energy vs carbon number



The reason for this unusual temperature dependence is due to the fact that the higher the carbon number the less it wants to add another carbon.

CDP10-L

Given: reduction of CO with hydrogen over Ni catalyst:

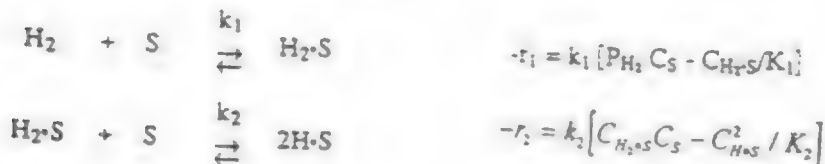


Kinetic given by:
$$r = \frac{0.0183 P_{\text{H}_2} P_{\text{CO}} \left(\frac{\text{gmole CH}_4}{\text{gm cat-min}} \right)}{1 + 1.5 P_{\text{H}_2}}$$

From the above expression:

- 1) The appearance of P_{H_2} in the denominator suggest that H_2 is adsorbed on the surface.
- 2) The fact that CO does not appear in the denominator suggests that it reacts as a gas phase species.
- 3) The square root dependence in the numerator suggests that H_2 splits.

Therefore, suggested mechanism is:





Remarks made in Chapter 5 of the text suggest that reaction 3 is rate controlling:

$$\frac{-r_1}{k_1} \equiv 0 \quad \text{CH}\cdot\text{S} = K_1 \text{P}_{\text{H}_2} \text{CS}$$

$$\frac{-r_2}{k_2} \equiv 0 \quad \text{CH}\cdot\text{S} = \sqrt{K_2 \text{CH}\cdot\text{S} \text{CS}} = \sqrt{K_1 K_2 \text{P}_{\text{H}_2} \text{CS}}$$

$$\frac{-r_5}{k_5} \equiv 0 \quad \text{C}\cdot\text{S} = \frac{\text{P}_{\text{CH}_4}}{K_5 \text{P}_{\text{H}_2}^2} \cdot \text{CS}$$

$$\frac{-r_4}{k_4} \equiv 0 \quad \text{CCHO}\cdot\text{S} = \frac{\text{C}\cdot\text{S} \text{PH}_2\text{O} \text{CS}}{K_4 \text{CH}\cdot\text{S}} = \frac{\text{P}_{\text{CH}_4} \text{PH}_2\text{O} \text{CS}}{K_4 K_5 \text{P}_{\text{H}_2}^2 \text{CH}\cdot\text{S}} = \frac{\text{P}_{\text{CH}_4} \text{PH}_2\text{O} \text{CS}}{K_4 K_5 \sqrt{K_1 K_2} \text{P}_{\text{H}_2}^2}$$

$$-r_3 = k_3 \left[\text{CH}\cdot\text{S} \text{PCO} - \frac{\text{CCHO}\cdot\text{S}}{K_3} \right] = k_3 \left[\sqrt{K_1 K_2 \text{P}_{\text{H}_2} \text{CS}} \text{PCO} - \frac{\text{P}_{\text{CH}_4} \text{PH}_2\text{O} \text{CS}}{K_3 K_4 K_5 \sqrt{K_1 K_2} \text{P}_{\text{H}_2}^2} \right]$$

$$\text{or } (-r_3) = \frac{k_3 \sqrt{K_1 K_2}}{\text{P}_{\text{H}_2}^2} \text{CS} \left[\text{P}_{\text{H}_2}^2 \text{PCO} - \frac{\text{P}_{\text{CH}_4} \text{PH}_2\text{O}}{K_1 K_2 K_3 K_4 K_5} \right]$$

$$\text{C}_\text{T} = \text{CS} + \text{CH}\cdot\text{S} + \text{C}\cdot\text{S} + \text{CCHO}\cdot\text{S}$$

$$\text{C}_\text{T} = \text{CS} \left[1 + K_1 \text{P}_{\text{H}_2} + \sqrt{K_1 K_2 \text{P}_{\text{H}_2}} + \frac{\text{P}_{\text{CH}_4}}{K_5 \text{P}_{\text{H}_2}^2} - \frac{\text{P}_{\text{CH}_4} \text{PH}_2\text{O}}{\text{P}_{\text{H}_2}^2 K_4 K_5 \sqrt{K_1 K_2}} \right]$$

Kinetic expression becomes

$$-r_3 = \frac{k_3 \sqrt{K_1 K_2} \text{C}_\text{T} \left[\text{P}_{\text{H}_2}^2 \text{PCO} - \frac{\text{P}_{\text{CH}_4} \text{PH}_2\text{O}}{K_1 K_2 K_3 K_4 K_5} \right]}{\left[\text{P}_{\text{H}_2}^2 + K_1 \text{P}_{\text{H}_2} + \sqrt{K_1 K_2 \text{P}_{\text{H}_2}} + \frac{\text{P}_{\text{CH}_4} \sqrt{\text{P}_{\text{H}_2}}}{K_5} + \frac{\text{P}_{\text{CH}_4} \text{PH}_2\text{O}}{K_4 K_5} \right]}$$

Reaction is irreversible \therefore let $K_5 \rightarrow \infty$ Then

$$-r_3 = \frac{k_3 \sqrt{K_1 K_2} \text{C}_\text{T} \text{P}_{\text{H}_2}^2 \text{PCO}}{\text{P}_{\text{H}_2}^2 [1 + K_1 \text{P}_{\text{H}_2} + \sqrt{K_1 K_2 \text{P}_{\text{H}_2}}]} = \frac{k_3 \sqrt{K_1 K_2} \text{C}_\text{T} \text{P}_{\text{H}_2}^2 \text{PCO}}{1 + K_1 \text{P}_{\text{H}_2} + \sqrt{K_1 K_2 \text{P}_{\text{H}_2}}}$$

with $K_1 \text{P}_{\text{H}_2} \gg \sqrt{K_1 K_2 \text{P}_{\text{H}_2}}$, we get

$$-r_3 = \frac{k_3 \sqrt{K_1 K_2} \text{C}_\text{T} \text{P}_{\text{H}_2}^2 \text{PCO}}{1 + K_1 \text{P}_{\text{H}_2}}. \text{ This expression implies that at moderate pressures, most of the active sites are occupied by the H}_2 \text{ molecules.}$$

- (a) Design for a plug flow reactor. Denote A[=] CO, B[=] H₂, then $y_{A0} = 0.25$, $y_{B0} = 0.75$, $\theta_B = \frac{F_{B0}}{F_{A0}} = \frac{y_{B0}}{y_{A0}} = 3$, $X_F = 0.80$

$$\delta = 1 + 1 - 2 = -1 \quad ; \quad \epsilon = y_{A0} \delta = -0.75$$

$$F_{A0} X_F = F_{CH_4} = 2000 \frac{\text{lb}}{\text{day}} \times \frac{\text{lbmole}}{16 \text{ lb}} = 125 \frac{\text{lbmole}}{\text{day}}$$

$$F_{A0} = \frac{125 \text{ lbmole}}{0.8 \text{ day}} = 156.25 \frac{\text{lbmole}}{\text{day}}$$

$$\text{Design equation } F_{A0} dX = -r_A dW \text{ or } \frac{W}{F_{A0}} = \int_0^{X_F} \frac{dX}{-r_A}$$

$$-r_A = \frac{0.0183 P_A P_B^2}{1 + 1.5 P_B}$$

$$P_A = C_A RT = \frac{C_{A0} RT (1-X)}{1 + \epsilon X} = \frac{y_{A0} P_0 (1-X)}{1 + \epsilon X}$$

$$P_B = C_B RT = \frac{C_{A0} RT (\theta_B - 3X)}{1 + \epsilon X} = \frac{C_{A0} RT (3 - 3X)}{1 + \epsilon X} = \frac{3 y_{A0} P_0 (1-X)}{1 + \epsilon X}$$

$$\therefore -r_A = \frac{0.0183 \left[\frac{y_{A0} P_0 (1-X)}{1 + \epsilon X} \right] \left[\frac{3 y_{A0} P_0 (1-X)}{1 + \epsilon X} \right]^{1/2}}{1 + 1.5 \left[\frac{y_{A0} P_0 (1-X)}{1 + \epsilon X} \right]} = \frac{0.0183 \sqrt{3} \left[\frac{y_{A0} P_0 (1-X)^{3/2}}{1 + \epsilon X} \right]}{1 + 1.5 \left[\frac{y_{A0} P_0 (1-X)}{1 + \epsilon X} \right]}$$

$$\therefore \frac{W}{F_{A0}} = \int_0^{X_F} \left(\frac{1 + 1.5 \left[\frac{y_{A0} P_0 (1-X)}{1 + \epsilon X} \right]}{0.0183 \sqrt{3} \left[\frac{y_{A0} P_0 (1-X)^{3/2}}{1 + \epsilon X} \right]} \right) dX$$

$$\frac{W}{F_{A0}} = \frac{1}{0.0183 \sqrt{3} (y_{A0} P_0)^{3/2}} \int_0^{X_F} \left[\left(\frac{1 + \epsilon X}{1-X} \right)^{3/2} + 1.5 y_{A0} P_0 \left(\frac{1 - \epsilon X}{1-X} \right)^{1/2} \right] dX$$

$$\frac{W}{F_{A0}} = \frac{1}{0.0183 \sqrt{3} (y_{A0} P_0)^{3/2}} \int_0^{0.8} \left[\left(\frac{1 + (-0.25)X}{1-X} \right)^{3/2} + 3.75 \left(\frac{1 - 0.25X}{1-X} \right)^{1/2} \right] dX$$

The integral can be solved using Simpson's rule

$$\text{Let } f(X) = \left[\frac{1 - 0.25X}{1-X} \right]^{3/2} + 3.75 \left[\frac{1 - 0.25X}{1-X} \right]^{1/2} = \left[\frac{1 - 0.25X}{1-X} + 3.75 \right] \left[\frac{1 - 0.25X}{1-X} \right]^{1/2}$$

$$\text{Then } \int_0^{X_F} f(X) dX \approx \frac{\Delta X}{3} [f(0) + \Delta f(0.2) + 2f(0.4) + 4f(0.6) + f(0.8)]$$

X	1-X	1-0.25X	$\frac{1-0.25X}{1-X}$	$\frac{1-0.25X}{1-X} + 3.75$	$\left(\frac{1-0.25X}{1-X}\right)^{1/2}$	f(X)	W	Wf(X)
0	1	1	1	4.750	1.000	4.750	1	4.750
0.2	0.8	0.95	1.1875	4.974	1.090	5.420	4	21.679
0.4	0.6	0.90	1.500	5.250	1.225	6.430	2	12.860
0.6	0.4	0.85	2.125	5.875	1.458	8.564	4	34.257
0.8	0.2	0.80	4.000	7.950	2.000	15.500	1	15.500

$$\int_0^{0.8} f(X) dX = \frac{0.2}{3} [4.750 + 21.679 + 12.860 + 34.257 + 15.500] = 5.936$$

$$W = \frac{5.936}{0.0183 \sqrt{3} (0.25 \times 10)^{3/2}} \frac{\text{gm cat} \cdot \text{min}}{\text{gmol}} \times \frac{156.25 \text{ lbmol}}{\text{day}} \times \frac{454 \text{ gmol}}{\text{lbmol}} \times \frac{1 \text{ day}}{24 \times 60 \text{ min}}$$

$$W = 2334 \text{ g}$$

(b) Design of a CSTR

Design equation is $W = \frac{F_{A0} X_F}{-r_A}$

$$W = \frac{F_{A0} X_F}{0.0183 \sqrt{3} (y_{A0} P_0)^{3/2} \left[\left(\frac{1+EX}{1-X} \right)^{3/2} + 1.5 y_{A0} P_0 \left(\frac{1+EX}{1-X} \right)^{1/2} \right]}$$

$$W = \frac{125 \text{ lbmol/day} \times 0.8}{0.0183 \sqrt{3} (0.25 \times 10)^{3/2} \left[\left(\frac{1+(25)(.8)}{1-.8} \right)^{3/2} + (1.5)(.25)(10) \left(\frac{1+(25)(.8)}{1-.8} \right)^{1/2} \right]} \frac{\text{gmcat} \cdot \text{min}}{\text{gmol}}$$

$$W = 12371 \frac{\text{lbmol}}{\text{day}} \times \frac{\text{gm cat} \cdot \text{min}}{\text{gmol}} \times \frac{454 \text{ gmol}}{\text{lbmol}} \times \frac{1 \text{ day}}{24 \times 60 \text{ min}}$$

$$W = 3900 \text{ g}$$

CDP10-M

(a) $a = 0$ at the end of the reactor.

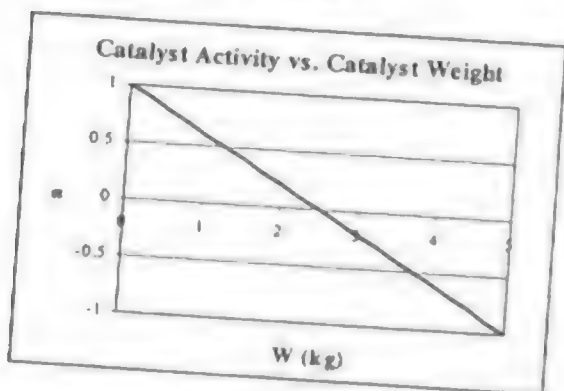
$$-\frac{da}{dW} = \frac{k_D}{U_s}$$

$$\int_1^0 -da = \frac{k_D}{U_s} \int_0^W dW \Rightarrow 1-a = \frac{k_D}{U_s} W$$

$$1-0 = \left(\frac{0.2 \text{ s}^{-1}}{U_s} \right) (5 \text{ kg}) \Rightarrow U_s = 1 \text{ kg/s}$$

(b) For $U_s = 0.5 \text{ kg/s}$:

$$a = 1 - \frac{k_D}{U_s} W = 1 - \left(\frac{0.2 \text{ s}^{-1}}{0.5 \text{ kg/s}} \right) W = 1 - (0.4 \text{ kg}^{-1}) W$$



When $a = 0$, the catalyst is inactive. In theory a can be negative, but in reality, once the catalyst is inactive there can be no further decrease in activity.

(c) For a catalyst feed rate of $U_s = 0.5 \text{ kg/s}$:

Mole Balance: $F_{A0} \frac{dX}{dW} = a(-r'_A)$

Rate Law: $-r'_A = kC_A C_B$

Decay Law: $-\frac{da}{dW} = \frac{k_D}{U_s} = \frac{0.2 \text{ s}^{-1}}{0.5 \text{ kg/s}} = 0.4 \text{ kg}^{-1} \Rightarrow a = 1 - 0.4W$

Stoichiometry: (Assume $T = T_0$, $P = P_0$, and $v = v_0$)
 $C_A = C_B = C_{A0}(1 - X)$

Combine:

$$F_{A0} \frac{dX}{dW} = (1 - 0.4W) [kC_{A0}^2 (1 - X)^2]$$

$$\left(\frac{F_{A0}}{kC_{A0}^2} \right) \frac{dX}{(1 - X)^2} = \left(1 - \frac{k_D}{U_s} W \right) dW \Rightarrow \left(\frac{F_{A0}}{kC_{A0}^2} \right) \frac{X}{(1 - X)} = \left(W - \frac{k_D}{2U_s} W^2 \right)$$

$$\frac{X}{(1 - X)} = \frac{kC_{A0}^2}{F_{A0}} \left(W - \frac{k_D}{2U_s} W^2 \right)$$

From part (b) we know that the maximum catalyst weight (the point where $a = 0$) is 2.5 kg. We will find the conversion at this point:

$$\frac{X}{(1 - X)} = \frac{(1)(0.2)^2}{0.2} \left(2.5 - \frac{(0.2)}{2(0.5)} 2.5^2 \right) = 0.25$$

$$X = 0.2$$

(d) To achieve 40% conversion:

$$\frac{X}{(1-X)} = \frac{kC_{A0}^2}{F_{A0}} \left(W - \frac{k_D}{2U_s} W^2 \right)$$

$$\frac{0.40}{(1-0.40)} = 0.2 \left(5 - \frac{0.2}{2U_s} 5^2 \right) \Rightarrow 0.667 = 1 - \frac{2.5}{U_s}$$

$$U_s = 7.5 \text{ kg/s}$$

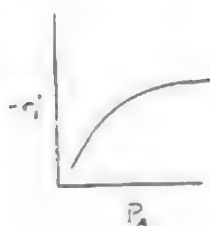
(e)

$$\text{For } U_s = \infty: \quad \frac{X}{(1-X)} = \frac{kC_{A0}^2}{F_{A0}} \left(W - \frac{k_D}{2(\infty)} W^2 \right) \Rightarrow \frac{X}{(1-X)} = \frac{kC_{A0}^2}{F_{A0}} (W)$$

$$\frac{X}{(1-X)} = (0.2)W = (0.2)(5) = 1 \Rightarrow X = 0.50$$

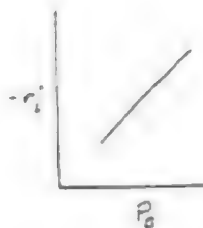
CDP10-N

(a)



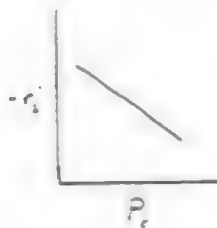
Runs 1, 3, 6, 7

$$-r_s = \frac{P_A}{1 + K_A P_A + \dots}$$



Runs 1, 2, 4

$$-r_s = P_B + \dots$$



Runs 4, 5

$$-r_s = \frac{1}{1 + K_C P_C + \dots}$$

(b) Numerator: P_A and P_B Denominator: P_A and P_C

Power of Denominator: 1

$$(c) \text{ Proposed Rate Law: } -r_s = \frac{k P_A P_B}{1 + K_A P_A + K_C P_C}$$

CDP10-N (cont'd)

- (d) To find the rate law parameters, rearrange the rate law so that it can be plotted as a line with the rate law parameters as the slope and intercept of the line.

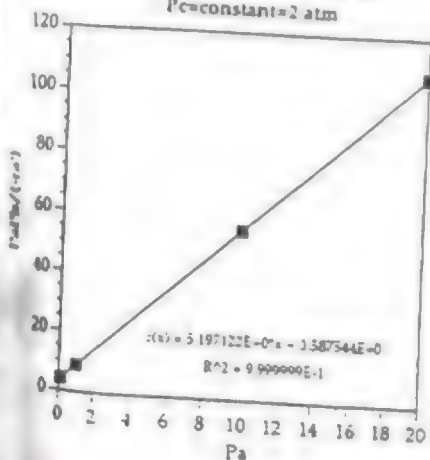
$$\frac{P_A P_B}{-r_s} = \frac{K_A}{k} P_A + \frac{K_C}{k} P_C + \frac{1}{k}$$

First, hold P_C constant and plot $\frac{P_A P_B}{-r_s}$ vs. P_A

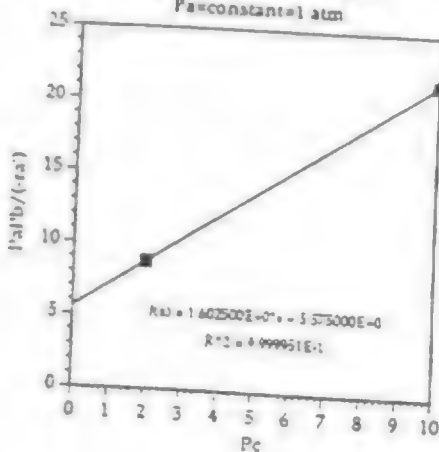
From the plot

$$\text{Slope} = \frac{K_A}{k} = 5.2, \quad y\text{-Intercept} = \frac{1 + K_C P_C}{k} = 3.59$$

Parameter Evaluation with
 $P_C = \text{constant} = 2 \text{ atm}$



Parameter Evaluation with
 $P_A = \text{constant} = 1 \text{ atm}$



Second, hold P_A constant and plot $\frac{P_A P_B}{-r_s}$ vs. P_C

From plot below,

$$\text{Slope} = \frac{K_C}{k} = 1.6025, \quad y\text{-Intercept} = \frac{1 + K_A P_A}{k} = 5.575$$

Using the four equations above to solve for k , K_A , and K_C , we get:

$$k = 2.60 \frac{\text{mol}}{\text{gcat} \cdot \text{sec} \cdot \text{atm}}, \quad K_A = 13.52 \text{ atm}^{-1}, \quad K_C = 4.1665 \text{ atm}^{-1}$$

10-89

(e) A and C are adsorbed on the surface of the catalyst.

(f) Proposed Mechanism:



The irreversible reaction step was assumed to be the limiting step. We check this mechanism and rate limiting step by rearranging and combining the rate laws for each step. If the mechanism is correct, we will obtain the rate law proposed in part c.

$$-r_A = k_A \left[P_A C_v - \frac{C_{A \cdot S}}{K_A} \right]$$

$$-r_s = k_s C_{A \cdot S} P_B$$

$$-r_C = k_C \left[C_{C \cdot S} - \frac{P_C C_v}{K_C} \right]$$

k_s is much smaller than k_A and k_C , therefore, $\frac{-r_A}{k_A} = \frac{-r_C}{k_C} = 0$

$$C_{A \cdot S} = K_A P_A C_v \quad \text{and} \quad C_{C \cdot S} = \frac{P_C C_v}{K_C} = K_C P_C C_v, \quad \text{where } K_C = \frac{1}{K_C}$$

$$\text{Also, } C_T = C_v + C_{A \cdot S} + C_{C \cdot S}$$

$$\text{After substitution, } C_v = \frac{C_T}{1 + K_A P_A + K_C P_C}$$

Next, substitute the above equations into the reactions step to get

$$-r_s = \frac{k P_A P_B}{1 + K_A P_A + K_C P_C}$$

Because this is the same as the rate law in part c, the rate law and limiting step assumptions have been verified.

CDP10-N (cont'd)

(g) Ratio of sites of A to sites of B at 80% conversion:

$$\frac{C_{A,s}}{C_{B,s}} = \frac{K_A P_A C_v}{K_B P_B C_v} = \frac{K_A P_{A,0}(1-X)}{K_B P_{A,0} X} = \frac{(13.52)(0.20)}{(4.1665)(0.80)} = 0.81$$

Conversion at which the number of sites of A equal the number of sites of C.

$$\frac{C_{A,s}}{C_{C,s}} = \frac{K_A(1-X)}{K_C X} = \frac{(13.52)(1-X)}{(4.1665)(X)} = 1$$

$$X = 0.76$$

(Solution by J.T. Santini, Jr.)

CDP10-O

- a) To determine the mechanism and rate-limiting step we must come up with the rate law. Looking at the rate dependence of A we see that between runs 1 and 2, P_A increases from 1 to 1000 atm while the rate law only increases from 1 to 1.5. This tells us that as A gets larger it changes the rate law a good deal less. This tells us that A is both in the numerator and the denominator.

$$-r'_A \sim \frac{P_A}{1 + K_A P_A}$$

Looking at the rate dependence of B we see that between runs 1 and 3, P_B increases from 1 to 4.5. This tells us that the rate law is directly related to B.

$$-r'_A \sim P_B$$

Looking at the rate dependence of C we see that between runs 7 and 9 P_C increases from 0 to 4 atm and the rate increases from 4.5 to 4.8. Also in these runs we see that P_A increases from 1 to 4 atm. So one of two things is true either P_C is both in the numerator and denominator or just in the denominator. Since C is a product it will not be in the numerator in an irreversible reaction.

$$-r'_A \sim \frac{P_B}{1 + K_C P_C}$$

So the rate law becomes

$$-r'_A = \frac{k P_A P_B}{1 + K_A P_A + K_C P_C}$$

10-91

With that rate law the following mechanism exists:

Adsorption



Surface reaction

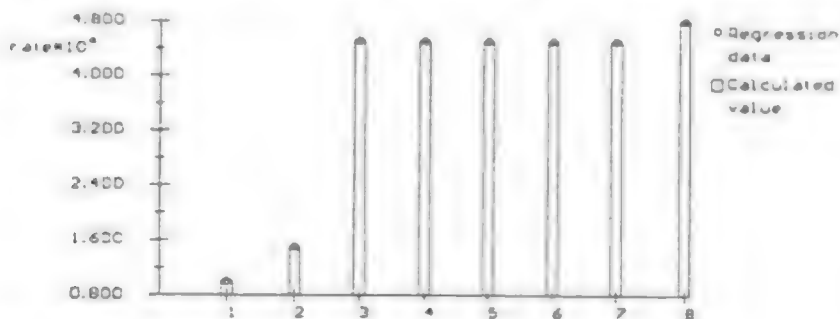


Dissociation



The surface reaction is the rate-limiting step.

- b) In evaluating the parameters we can also see if our rate law is a good one. Plugging into POLYMATH we can come up with the parameters.



Model: $rate = k P_A P_B / (1 + K_A P_A + K_C P_C)$

$k = 0.00049997$

$K_C = 0.5$

$K_A = 2.99989$

4 positive residuals, 4 negative residuals. Sum of squares = 5.26309e-15

We find that the rate law is a good one.

$$k = 0.00045$$

$$K_A = 3$$

$$K_C = .5$$

- c) The best places to add points would be where P_C is changed, but P_A and P_B are not changed.
- d) No solution will be given.

CDP10-P (cont'd)

Using point 10, $P = 0$

$$\therefore K_4 = 0.0399$$

Check

Using point 11, $P_E = 0 \Rightarrow K_4 = 0.0368$, close enough

Using point 6, $P_W = 0 \Rightarrow K_3 = 0.659$

Finally, using point 12 $\Rightarrow K_{eq} = 0.0975$

$$r = \frac{0.0409 (P_A^2 - 10.256 P_E P_W)}{[1 + 17.31 P_A + 1.517 P_E + 25.05 P_W]^2}$$

Note: K_{eq} may also be calculated using $RT \ln K_{eq} = -\Delta G^\circ$. Interested readers are encouraged to check the goodness of fit of this rate law with the data.

CDP10-Q

Design Equation : $N_{B0} \frac{dX}{dt} = -r'_A aW$

Rate Law : $-r'_B = k' C_B^2$

Decay Law : $-\frac{da}{dt} = k_D = 0.05$

$$\int_1^0 da = -0.05 \int_0^t dt \Rightarrow a = 1 - 0.05t$$

From this we can see that the maximum reaction time is 20 min. We will find the conversion at this point.

Stoichiometry : (Assume constant volume)

$$C_B = C_{B0} (1 - X) = \frac{N_{B0}}{V} (1 - X)$$

Combine : $\frac{dX}{dt} = \frac{k' (1 - 0.05t) N_{B0}^2 (1 - X)^2 W}{V^2 N_{B0}} = \frac{k' W N_{B0}}{V^2} (1 - 0.05t) (1 - X)^2$

$$\frac{dX}{(1 - X)^2} = \frac{k' W N_{B0}}{V^2} (1 - 0.05t) dt \Rightarrow \frac{X}{1 - X} = \frac{k' W N_{B0}}{V^2} (t - 0.025t^2)$$

$$\frac{X}{1 - X} = \frac{(0.01)(10)(1)}{(1)} (20 - 0.025(20)^2) = 1$$

$$X = 0.50$$

10 - 94

P10-R

a) Mole balances:

$$\frac{dF_A}{dW} = r_A \quad \frac{dF_B}{dW} = r_B \quad \frac{dF_C}{dW} = r_C$$

rate laws:

$$-r'_A = ak_1 C_A \quad -r'_B = a(k_2 C_B - k_1 C_A) \quad r'_C = ak_2 C_B$$

stoichiometry:

$$C_A = \frac{F_A}{v} = \frac{F_A(1 - \alpha W)^{0.5}}{v_0}$$

$$C_B = \frac{F_B}{v} = \frac{F_B(1 - \alpha W)^{0.5}}{v_0}$$

decay law:

$$-\frac{da}{dW} = \frac{k_D a}{U_s}$$

Evaluate the parameters:

$$k_1 = 0.02 * \exp\left[\frac{10000}{1.987} \left(\frac{1}{400} - \frac{1}{T}\right)\right]$$

$$k_2 = 0.01 * \exp\left[\frac{20000}{1.987} \left(\frac{1}{400} - \frac{1}{T}\right)\right]$$

$$k_D = 0.08 * \exp\left[\frac{15000}{1.987} \left(\frac{1}{400} - \frac{1}{T}\right)\right]$$

Plugging all of this into POLYMATH we can change values of U_s , T , and v_0 (P_{A0}) that will give us the most of product B.

We find that at a temperature of 396K, a solids velocity of 10kg/s and a gas volumetric velocity of 0.633 dm³/s that corresponds to a partial pressure of 51.3 atm we can the maximum yield for B.

Equations:

$$d(fa)/d(w)=ra$$

$$d(fb)/d(w)=rb$$

$$d(fc)/d(w)=rc$$

$$d(a)/d(w)=kd*a/Us$$

$$Us=10$$

$$T=396$$

$$alp=9.8e-3$$

$$vo=.633$$

$$kd=.08*exp(15000/1.987*(1/400-1/T))$$

$$k2=.01*exp(20000/1.987*(1/400-1/T))$$

$$k1=.02*exp(10000/1.987*(1/400-1/T))$$

$$ca=fa*(1-alp*w)^.5/vo$$

$$cb=fb*(1-alp*w)^.5/vo$$

$$ra=-a*k1*ca$$

$$rc=a*k2*cb$$

$$rb=-a*(k2*cb-k1*ca)$$

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	100	0	100
fa	1	1	0.0013942	0.0013942
fb	0	0.524458	0	0.446634
fc	0	0.471971	0	0.471971
a	1	1.93702	1	1.93702
Us	10	10	10	10
T	396	396	396	396
alp	0.0098	0.0098	0.0098	0.0098
vo	0.633	0.633	0.633	0.633
kd	0.0661149	0.0661149	0.0661149	0.0661149
k2	0.00775554	0.00775554	0.00775554	0.00775554
k1	0.0176131	0.0176131	0.0176131	0.0176131
ca	1.57978	1.57978	0.0161846	0.0161846
cb	0	0.61042	0	0.0997846
ra	-0.0278248	-0.000427403	-0.0278248	-0.000427403
rc	0	0.00641366	0	0.00149902
rb	0.0278248	0.0278248	-0.00217423	-0.000418621

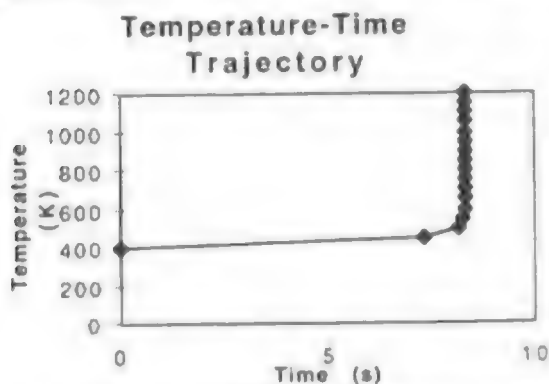
b) Using the same program we can find what it takes to get the most of C possible. We find that at $T = 396K$, $U_1 = 10$, and $v_0 = .03$ we can get 1 mol C/s. $P_{A0} = 1082.4$ atm.

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	100	0	100
fa	1	1	1.02629e-23	1.02629e-23
fb	0	0.524487	0	1.75043e-10
fc	0	1	0	1
a	1	1.93702	1	1.93702
Us	10	10	10	10
T	396	396	396	396
alp	0.0098	0.0098	0.0098	0.0098
vo	0.03	0.03	0.03	0.03
kd	0.0661149	0.0661149	0.0661149	0.0661149
k2	0.00775554	0.00775554	0.00775554	0.00775554
k1	0.0176131	0.0176131	0.0176131	0.0176131
ca	33.3333	33.3333	4.83798e-23	4.83798e-23
cb	0	17.2696	0	6.36595e-10
ra	-0.587104	-1.65057e-24	-0.587104	-1.65057e-24
rc	0	0.13615	0	9.5632e-10
rb	0.587104	0.587104	-0.0716782	-9.56321e-10

c) To get the Time-Temperature trajectory we can use the following equation to create it:

$$t = \frac{1 - \exp\left[\frac{E_d}{R}\left(\frac{1}{T} - \frac{1}{400}\right)\right]}{k_{d0}(E_d/E_A)}$$

This will give us the following graph:



d) For this we just add an energy balance. We have to assume a heat capacity of the catalyst since none is given. Here it is assumed to be 100 J/kgcat.

$$\frac{dT}{dW} = \frac{(r'_A)(\Delta H_{R1}) + (r'_B)(\Delta H_{R2})}{C_{p1}U_s + C_p(F_A + F_B + F_C)}$$

Plugging this into the POLYMATH gives the following program.

We find that the temperature is 388K, $U_s = 10$ kg/s and $v_o = 0.51$ dm³/s. $P_{A0} = 62.4$ atm.

Equations:	Initial value	Variable	Initial value	Maximum value	Minimum value	Final value
$d(fa)/d(w)=ra$	1	w	0	100	0	100
$d(fb)/d(w)=rb$	0	fa	1	1	0.173516	0.173516
$d(fc)/d(w)=rc$	0	fb	0	0.611156	0	0.611156
$d(a)/d(w)=kd*a/Us$	1	fc	0	0.215328	0	0.215328
$d(T)/d(w)=(ra*(-16000)+rb*(-32000))/(cp*(Us+fa+fb+fc))$	388	a	1	1.40401	1	1.40401
$kd=.08*\exp(15000/1.987*(1/400-1/T))$		T	388	388	381.464	382.242
$Us=10$		kd	0.0446269	0.0446269	0.0319753	0.0332906
$cp=100$		Us	10	10	10	10
$k2=.01*\exp(20000/1.987*(1/400-1/T))$		cp	100	100	100	100
$k1=.02*\exp(10000/1.987*(1/400-1/T))$		ka	0.00459207	0.00459207	0.00294419	0.00310677
$alp=9.8e-3$		k1	0.011553	0.011553	0.0108521	0.0111477
$vo=.51$		alp	0.0098	0.0098	0.0098	0.0098
$ca=fa*(1-alp*w)^.5/vo$		vo	0.51	0.51	0.51	0.51
$cb=fb*(1-alp*w)^.5/vo$		ca	1.96078	1.96078	0.0481154	0.0481154
$ra=-a*k1*ca$		cb	0	0.783935	0	0.169472
$rc=a*k2*cb$		ra	-0.0265744	-0.0265744	-0.0265744	-0.000753076
$rb=-a*(k2*cb-k1*ca)$		rc	0	0.0023258	0	0.000719224
$v_o = 0, \quad w_f = 100$		rb	0.0265744	0.0265744	1.38516e-05	1.38516e-05

P11-1

No solution will be given.

Problem P11-2_B

Part (a)

No solution will be given.

Part (b)

No difference.

Part (c)

No difference except on physical property data.

Part (d)

The growing core model would have the same molar flux as the shrinking core

$$W_A = - \frac{De \cdot C_{AO}}{\left(\frac{1}{R(t)} - \frac{1}{R_0} \right)} r^2$$

but $R(t)$, the radius of the carbon interface will increase with time rather than decrease.

The rate of appearance of carbon is equal to the flux of oxygen to the gas-carbon interface

$$r_c'' = -W_A|_{r=R} = - \frac{De \cdot C_{AO}}{\left(R - \frac{R^2}{R_0} \right)}$$

$$\text{and} \quad \frac{dR}{dt} = \frac{r_c''}{\phi_c \cdot \rho_c}$$

$$\frac{dR}{dt} = - \frac{De \cdot C_{AO}}{\phi_c \cdot \rho_c} \cdot \frac{1}{\left(R - \frac{R^2}{R_0} \right)}$$

as for the shrinking model but without the minus sign, because R increases with time.

P11-2 cont'd

Boundary conditions

$$t = 0$$

$$R = R_0$$

$$\int_{R_0}^R \left(R - \frac{R^2}{R_0} \right) dR = \frac{De \cdot C_{A0}}{\phi \cdot \rho_c} \int_0^t dt$$

$$\frac{R^2 - R_0^2}{2} - \frac{R^3 - R_0^3}{3R_0} = \frac{De \cdot C_{A0}}{\phi \cdot \rho_c} t$$

Part (e)

Liquid phase : e.g. water

$$Re = \frac{\rho \cdot u \cdot d}{\mu} = \frac{1000 \times 0.1 \times 0.05}{10^{-3}} = 5000$$

P11-2 cont'd

$$Sc = \frac{\mu}{\rho \cdot D_{AB}} = \frac{10e-3}{1000 \times 10e-9} = 1000$$

single spheres

$$Sh = 2 + 0.6Re^{1/2} Sc^{1/3} = 2 + 0.6(5000)^{1/2} (1000)^{1/3} \sim 400$$

$$kc = \frac{Sh \cdot D_{AB}}{dp} = \frac{400 \times 10e-9}{0.002} = 0.0002 m^2 / s$$

Gas phase : e.g. air

$$Re = \frac{\rho \cdot u \cdot d}{\mu} = \frac{1 \times 0.1 \times 0.05}{10e-5} = 500$$

$$Sc = \frac{\mu}{\rho \cdot D_{AB}} = \frac{10e-5}{1 \times 10e-9} = 1$$

$$Sh = 2 + 0.6Re^{1/2} Sc^{1/3} = 2 + 0.6(500)^{1/2} (1)^{1/3} = 15$$

$$kc = \frac{Sh \cdot D_{AB}}{dp} = \frac{15 \times 10e-5}{0.002} = 0.075 m^2 / s$$

Problem P11-3_a

Mol balance on oxygen : $F_{O_2} - 0 + r_{O_2} = 0$ constant liquid composition.

$F_{O_2} = CO_2 \cdot v_0$ and $r_{O_2} = -k \cdot CO_2^n$ where n is the reaction order.

Assuming ideal gas law applies : $F_{O_2} = \frac{P \cdot v_0}{R \cdot T}$ where v_0 = oxygen uptake rate mL/hr

Assuming that $\frac{P}{R \cdot T} = \text{constant}$, C by correction of v_0 to some reference,

then $F_{O_2} = C \cdot v_0$

Assuming Henry's law applies (low pressures) $CO_2 = H \cdot P_{O_2}$

where H is Henry's constant and P_{O_2} is the oxygen partial pressure

P11-3cont'd

Substituting into the mol balance : $F_{O_2} = -r_{O_2}$

$$C \cdot v_o = k \cdot C_{O_2}^n = k \cdot (H \cdot P_{O_2})^n$$

$$v_o = P_{O_2}^n \cdot \frac{k \cdot H^n}{C}$$

$$\ln v_o = n \cdot \ln P_{O_2} + \ln \frac{k \cdot H^n}{C}$$

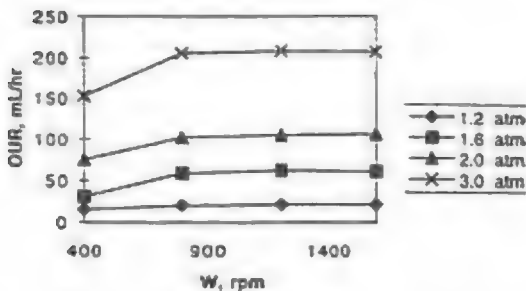
A plot of $\ln v_o$ vs $\ln P_{O_2}$ will give n as the gradient.

As the system pressure, P , given in the data is absolute : $P = P_i + P_{O_2}$

if in the reactor, the xylene is at boiling point and dissolved oxygen and oxidized xylene are at low levels, then $P_i = 1$ atm (open to the atmosphere)

In order to deduce the correct kinetics of the oxidation it is necessary to find the partial oxygen pressures for the conditions where the rate is limited only by the reaction kinetics and not by diffusional mass transfer.

Plot of stirrer speed, W , vs oxygen uptake rate, v_o , for each run will show the conditions at which diffusion is negligible.



It can be seen that at stirrer speeds above 1200 rpm that OUR is insensitive to W and hence the reactor is well mixed i.e. no liquid diffusional limitations.

OUR: Oxygen Uptake Rate

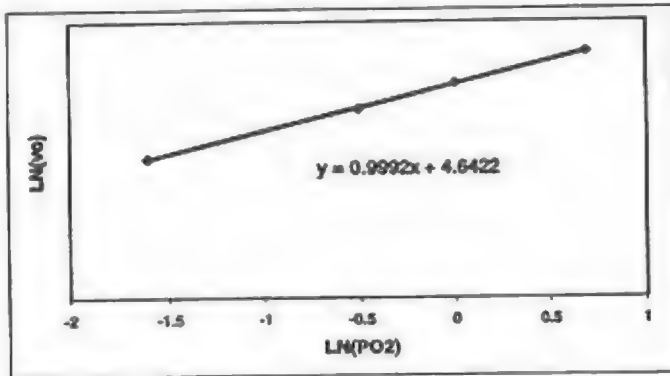
Hence using the system pressure data at 1600 rpm for the plot of $\ln v_o$ vs $\ln P_{O_2}$ will give n uninfluenced by diffusion.

$$P_{O_2} = P - P_i = P - 1$$

P11-3 cont'd

At 1600 rpm

v_o , ml/hr	$\ln v_o$	P_{O_2} atm	$\ln P_{O_2}$
21	3.04	0.2	-1.61
61	4.11	0.6	-0.51
106	4.66	1.0	0.00
207	5.33	2.0	0.69



The gradient, $n = .999 = 1$, so the rate law is:

$$-r_{O_2} = k.C_{O_2}^1$$

Problem P11-4g

Part (a & b)

Packed bed, mass transfer limited, gas phase

Mol balance : $-\frac{1}{Ac} \frac{dFa}{dz} + ra'' \cdot a_c = 0$ where $Fa = U.Ca.Ac$

$$\frac{1}{Ac} \frac{FaodX}{dz} = ra'' \cdot a_c$$

$$\frac{U.Cao.dX}{dz} = ra'' \cdot a_c \quad U = \text{constant superficial gas velocity}$$

Rate law :

Mass transfer limited boundary condition

$$ra'' = kc.(Ca - Cas) \quad \text{but } Cas = 0, \text{ rapid reaction}$$

P11-4 cont'd

Stoichiometry :

Assume constant T, P, gas phase

$$C_a = \frac{C_{ao}(1-X)}{(1+\epsilon.X)} \quad \text{where } \epsilon = y_{ao}\delta = 0.05 \times 3 = 0.15$$

Combining :

$$\frac{U.C_{ao}.dX}{dz} = ra'' . a_c$$

$$C_{ao}.U_o.\frac{dX}{dz} = a_c.kc.C_a$$

$$\frac{dX}{dz} = \frac{a_c.kc.(1-X)}{U_o.(1+0.15X)}$$

Use Thoenes & Kramers correlation for kc :

$$Sh' = (Re')^{1/2} (Sc')^{1/3}$$

$$\frac{kc.dp}{Dab} \cdot \left(\frac{\phi}{1-\phi} \right) \cdot \frac{1}{\gamma} = \left[\frac{U.dp.\rho}{\mu.(1-\phi).\gamma} \right]^{1/2} \left[\frac{\mu}{\rho.Dab} \right]^{1/3}$$

Parameter evaluation :

$$d_p = \left[\frac{6}{\pi} V_p \right] = \left[\frac{6(0.5)^2 0.5}{\pi} \right] = 0.238 \text{ cm}$$

Diffusion of cyclohexane in hydrogen (assuming constant T, P)

$$Dab = \frac{0.0017^{1.75} \left[\frac{1}{Ma} + \frac{1}{Mb} \right]^{1/2}}{P \left[(\sum Va)^{1/3} + (\sum Vb)^{1/3} \right]^2}$$

Fuller, Schettler, Giddings for binary mixture, low pressure, non polar (Perry's handbook chem.eng.)

M_a, M_b = molecular masses = 84, 2 respectively

V_a, V_b = diffusion volumes = 122, 7.07 cm³/mol respectively

$$Dab = \frac{0.001(773)^{1.75} \left[\frac{1}{84} + \frac{1}{2} \right]^{1/2}}{2 \left[(\sum 122)^{1/3} + (7.07)^{1/3} \right]^2} = 0.857 \text{ cm}^2 / \text{s}$$

P11-4 cont'd

$$\phi = 0.4$$

$$\gamma = \frac{2\pi \cdot \frac{d^2}{4} + \pi \cdot d \cdot l \cdot \frac{0.5^2}{2} + 0.5(0.5)}{\pi \cdot d p^2} = \frac{0.572}{0.572} = 1.146$$

$$U_o = \frac{v_o}{Ac} = \frac{60000}{\frac{\pi \cdot d^2}{4} \cdot 60} = 50.9 \text{ cm/s}$$

$$U = U_o(1 + \epsilon \cdot X) = 50.9(1 + 0.15X)$$

$$\rho = \frac{RMM \cdot P}{R \cdot T} = \frac{(84 \times 0.05 \times 2) + (2 \times 0.95 \times 2)}{0.0821 \times 773} = 0.19 \text{ gm/l} = 0.00019 \text{ g/cm}^3$$

$$\mu = 0.00017 \text{ g/cm.s (H}_2\text{, 500 K, 2 atm)}$$

$$Re' = \frac{50.9(1 + 0.15X) \cdot 0.572 \times 0.00019}{0.00017(1 - 0.4) \cdot 1.146} = 47.3(1 + 0.15X)$$

$$Sc' = \frac{0.00017}{0.00019 \times 0.857} = 1.044$$

$$kc \cdot \frac{0.572}{0.857} \left(\frac{0.4}{1 - 0.4} \right) \cdot \frac{1}{1.146} = 0.388 \cdot kc$$

$$kc = \frac{1}{0.388} \cdot [47.3(1 + 0.15X)]^{1/2} [1.044]^{1/3} = 17.98(1 + 0.15X)^{1/2}$$

$$a_c = \frac{6(1 - 0.4)}{0.572} = 6.29 \text{ cm}^{-1}$$

$$\frac{dX}{dz} = 2.22 \frac{(1 - X)}{(1 + 0.15X)^2} \quad \text{POLYMATH}$$

P11-4 cont'd

Problem P11-4B part a/b

Equations:

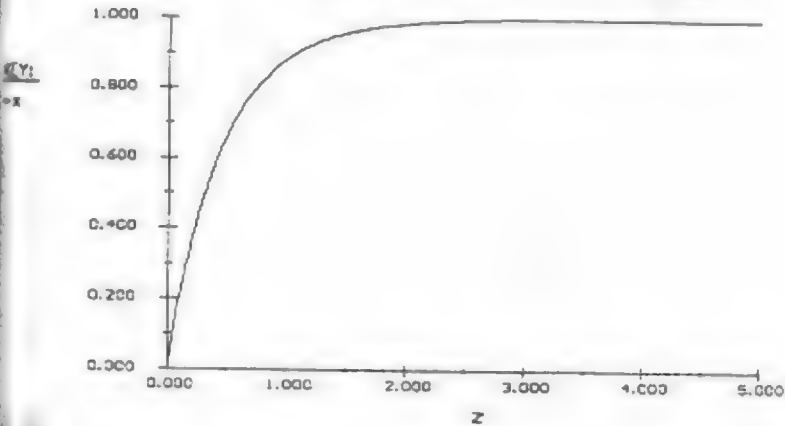
$$dx/dz = 2.22(1-x)/(1+0.15x)^{0.5}$$

Initial value

0

$$x = 0, \quad z_f = 5$$

Variable	Initial value	Maximum value	Minimum value	Final value
x	0	5	0	5
z	0	0.99997	0	0.99997



z	x
2.625	0.99591419
2.6875	0.99641018
2.75	0.99684594
2.8125	0.9972288
2.875	0.99756518
2.9375	0.99786072
3	0.99812039
3.0625	0.99834853
3.125	0.99854898
3.1875	0.9987251
3.25	0.99887983
3.3125	0.99901579
3.375	0.99913525
3.4375	0.9992402
3.5	0.99933242
3.5625	0.99941344

The results show that only 3.3 cm of the tube is required for conversion of 99.9%, much less than the full 20 m.

Part (c)

$$\frac{k_c \cdot dp}{D_{ab}} \left(\frac{\phi}{1-\phi} \right) \frac{1}{\gamma} = \left[\frac{U \cdot dp \cdot \rho}{\mu(1-\phi)\gamma} \right]^{1/2} \left[\frac{\mu}{\rho \cdot D_{ab}} \right]^{1/3}$$

Assuming the porosity remains the same, factors in the correlation affected by the size of the catalyst pellets are:

$$dp = \left[\frac{6}{\pi} \cdot V_p \right]^{1/3} = \left[\frac{6(0.25)^2 \cdot 0.25}{4} \right]^{1/3} = 0.286 \text{ cm}$$

$$\gamma = \frac{2 \cdot \pi \cdot \frac{d^2}{4} + \pi \cdot d \cdot l}{\pi \cdot dp^2} = \frac{\frac{0.25^2}{2} + 0.25(0.25)}{0.286} = 1.145$$

$$Re' = \frac{50.9(1+0.15X)0.286 \cdot 0.00019}{0.00017(1-0.4)1.145} = 23.68(1+0.15X)$$

$$k_c \cdot \frac{0.286}{0.857} \left(\frac{0.4}{1-0.4} \right) \frac{1}{1.145} = 0.194 \cdot k_c$$

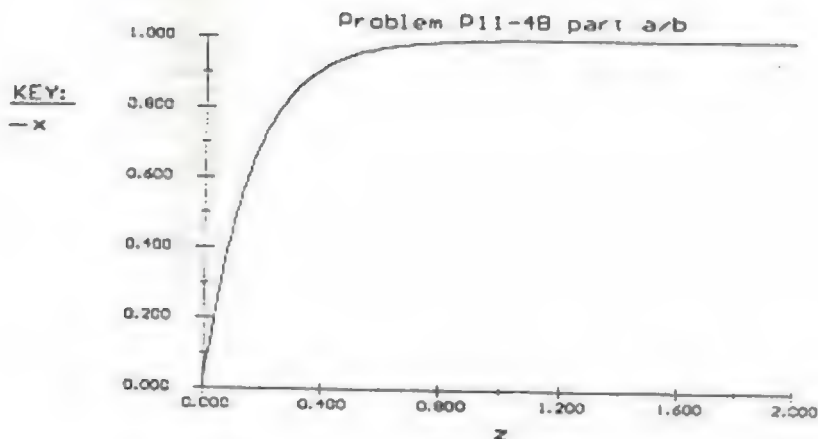
$$k_c = \frac{1}{0.194} \cdot [23.68(1+0.15X)]^{1/2} [1.044]^{1/3} = 25.39(1+0.15X)^{1/2}$$

$$a_c = \frac{6(1-0.4)}{0.286} = 12.59 \text{ cm}^{-1}$$

$$\frac{dX}{dz} = \frac{12.59 \cdot 25.39(1+0.15X)^{1/2}}{50.9} \cdot \frac{(1-X)}{(1+0.15X)}$$

$$\frac{dX}{dz} = 6.28 \frac{(1-X)}{(1+0.15X)^{1/2}} \quad \text{POLYMATH}$$

P11-4 cont'd



As can be seen from the above graph, the affect of reducing the dimensions of the pellets by half results in the conversion reaching 99.9 % 1.18 cm from the entrance. This seems reasonable because reducing the size of the catalyst particles is one of the methods for increasing mass transfer and hence k_c .

Part (d)

If pure cyclohexane feed were used at the same volumetric flowrate $60 \text{ dm}^3/\text{min}$, then the initial bulk concentration would be greater and there would be a greater concentration gradient across the stagnant film on the pellets. However the mass transfer coefficient will be reduced as the products must diffuse away from the surface which will be harder in higher concentrations of cyclohexane.

The equations used in Part (a) do not incorporate C_{A0} , the initial cyclohexane concentration (C_{A0} is cancelled out), so the only affect this change would have is to alter the physical properties of the bulk flow :

$$\rho = \frac{RMM \cdot P}{R \cdot T} = \frac{(84 \times 2)}{0.0821 \times 773} = 2.647 \text{ gm/l} = 0.00265 \text{ g/cm}^3$$

$$\mu = ? \text{ g/cm.s (cyclohexane , 500 K , 2 atm)}$$

Part (e)

This problem gives an indication as to how changes in parameters may affect a packed bed.

Problem P11-5_B

Mass transfer limited, rapid reaction, packed bed.

$$X_1 = 0.632 \quad \text{for } d_p, L_b \text{ and } u_0$$

$$X_2 = ? \quad \text{for } d_p/3, 1.5 L_b \text{ and } 4 u_0$$

$$X = 1 - \exp\left(-\frac{kc \cdot a_v \cdot L}{u}\right) \quad \text{or} \quad Ln\left(\frac{1}{1-X}\right) = \frac{kc \cdot a_v \cdot L}{u}$$

Thoenes and Kramers

$$Sh' = Re'^{1/2} Sc'^{1/3}$$

$$Re' = \frac{Re}{(1-\phi)\gamma} = \frac{\rho u d_p}{\mu(1-\phi)}$$

assume spheres ($\gamma = 1$) and constant fluid properties, voidage.

$$Sc' = \frac{\mu}{\rho \cdot D_{AB}}$$

$$Sh' = \frac{Sh \cdot \phi}{(1-\phi) \cdot \gamma} = \frac{kc \cdot d_p \cdot \phi}{D_{AB}(1-\phi)}$$

$$kc = \frac{D_{AB} \cdot (1-\phi)}{d_p \cdot \phi} \left(\frac{\rho \cdot u \cdot d_p}{1-\phi} \right)^{1/2} Sc'^{1/3}$$

$$kc \propto \frac{u^{1/2}}{d_p^{1/2}}$$

$$u = \frac{u_0}{A_b} \quad \text{constant bed diameter } u \propto u_0$$

$$a_v = \frac{6 \cdot (1-\phi)}{d_p}$$

$$a_v \propto \frac{1}{d_p}$$

$$Ln\left(\frac{1}{1-X}\right) \propto \left(\frac{u_0}{d_p}\right)^{1/2} \cdot \frac{1}{d_p} L \frac{1}{u_0} \propto \frac{1}{u_0^{1/2}} \cdot \frac{1}{d_p^{3/2}} \cdot L$$

$$\frac{Ln\left(\frac{1}{1-0.632}\right)}{Ln\left(\frac{1}{1-X_2}\right)} = \frac{(4u_0)^{1/2}}{u_0^{1/2}} \cdot \frac{\left(\frac{d_p}{3}\right)^{3/2}}{d_p^{3/2}} \cdot \frac{L}{1.5L} = 2 \left(\frac{u_0}{u_0}\right)^{1/2} \left(\frac{1}{3}\right)^{3/2} \left(\frac{d_p}{d_p}\right)^{3/2} \cdot \frac{1}{1.5}$$

$$= 0.257$$

$$Ln \frac{1}{1-X_2} = \frac{Ln \frac{1}{1-0.632}}{0.257} = 3.896$$

$$X_2 = 0.98$$

// - //

P11-5 cont'd

Proposed guidelines for optimum process conditions :

Use high T , so that the removal of chlorine is only mass transfer limited (i.e. rapid reaction rate of diffusion).

Increasing u (directly proportional to velocity u), enhances the mass transfer coefficient but also acts to reduce conversion X . The latter dependency is more influential on X (raised to a higher power), so reduction of u may be preferable (for constant packed bed properties). If conversion is already high enough, then a larger velocity may be preferable for a mass transfer limited reaction.

The mass transfer rate can be increased by increasing the concentration gradient achieved by increasing the bulk C_A .

Problem P11-6B

Mass transfer limited, packed bed, reversible reaction.

Part (a)

Assume a Langmuir-Hinshelwood mechanism surface reaction

$$-r_{A_s}'' = \frac{k_1 C_{A_s} - k_2 C_{B_s}}{1 + k_1 C_{A_s} + k_2 C_{B_s}}$$

at high T weak adsorption $1 \gg k_1 C_{A_s} + k_2 C_{B_s}$

$$-r_{A_s}'' = k_1 C_{A_s} - k_2 C_{B_s} = k_1 \left[C_{A_s} - \frac{C_{B_s}}{K} \right]$$

where equilibrium constant $K = \frac{k_1}{k_2}$

Mass transfer limited boundary conditions $W_A|_{\text{surface}} = k_{A_s}(C_A - C_{A_s}) = -r_{A_s}''$

$W_B|_{\text{surface}} = k_{B_s}(C_{B_s} - C_B) = -r_{A_s}''$

$$k_1 \left[C_{A_s} - \frac{C_{B_s}}{K} \right] = -r_{A_s}''$$

P11-6 cont'd

$$C_A - C_{A_s} = \frac{-r_{A_s}}{k_A} \quad (1)$$

$$C_B - C_{B_s} = \frac{-r_{A_s}}{k_B} \quad (2)$$

$$\left[C_A - \frac{C_{B_s}}{K} \right] = \frac{-r_{A_s}}{k_1} \quad (3)$$

(1) + (3) eliminates C_{A_s}

$$-r_{A_s}'' \left[\frac{1}{k_A} - \frac{1}{k_1} \right] = C_A + \frac{C_{B_s}}{K}$$

$$-r_{A_s}'' \left[\frac{1}{k_A} - \frac{1}{k_1} \right] \cdot K = K \cdot C_A + C_{B_s} \quad (4)$$

(2) + (4) eliminates C_{B_s}

$$-r_{A_s}'' \left[\left(\frac{1}{k_A} - \frac{1}{k_1} \right) \cdot K + \frac{1}{k_B} \right] = K \cdot C_A - C_B$$

$$-r_{A_s}'' \left[\left(\frac{1}{k_A} - \frac{1}{k_1} \right) + \frac{1}{K \cdot k_B} \right] = C_A - \frac{C_B}{K}$$

But it is mass transfer limited so k_1 is relatively large

$$-r_{A_s}'' \left[\frac{1}{k_A} + \frac{1}{K \cdot k_B} \right] = C_A - \frac{C_B}{K}$$

$$-r_{A_s}'' = \frac{C_A - \frac{C_B}{K}}{\left[\frac{1}{k_A} + \frac{1}{K \cdot k_B} \right]}$$

Gives

$$-r_{A_s}'' = \frac{k_B \left[C_A - \frac{C_B}{K} \right]}{\frac{k_B}{k_A} + \frac{1}{K}}$$

Part (b)

$$X_1 = X_2 \quad \ln\left(\frac{1}{1-X}\right) = \frac{k_c \cdot a_c \cdot L}{u}$$

Thoenes and Kramers $Sh' = Re'^{1/2} Sc'^{1/3}$

$Sh' \propto kc$ and $Re' \propto u$

$$\frac{k_{c1} \cdot a_{c1} \cdot L_1}{u_1} = \frac{k_{c2} \cdot a_{c2} \cdot L_2}{u_2}$$

$$k_c = \frac{D_{AB}(1-\phi)}{d_p \phi} \left(\frac{\rho u d_p}{\mu(1-\phi)} \right)^{1/2} \left(\frac{\mu}{\rho D_{AB}} \right)^{1/3}$$

$k_c \propto u^{1/2}$ all other parameters are constant

$a_{c1} = a_{c2} = \text{constant}$

$$\frac{L_1}{u_1^{1/2}} = \frac{L_2}{u_2^{1/2}}$$

if the flowrate is doubled and the diameter of the packed bed remains the same, then $u_2 = 2 u_1$

$$L_2 = (2u_1)^{1/2} \frac{L_1}{u_1^{1/2}} = 1.41 L_1$$

Hence the required catalyst weight W_2 will be $1.41 W_1$, the original catalyst weight, if the strategy is to increase bed length rather than diameter.

$$X = 1 - \exp\left(-\frac{k_c \cdot a_c \cdot L}{u}\right) \quad \text{let}$$

$$E = \left(\frac{k_c a_c L}{u} \right)$$

$$1 - \frac{1}{e^E} = X$$

E increases, e^E increases, $1/e^E$ decreases, X increases

P11-6 cont'd

If $u \uparrow$ then E and $X \downarrow$

Temperature, T , affects k_c (via D_{AB} , μ and ρ)

$$k_c \propto D_{AB} \left(\frac{\rho}{\mu} \right)^{1/2} \left(\frac{\mu}{\rho \cdot D_{AB}} \right)^{1/3} \quad \text{from T-K correlation}$$

$$\text{hence } E \propto \frac{D_{AB}^{2/3} \rho^{1/6}}{\mu^{1/6}}$$

If $T \uparrow$ then $\mu \downarrow$ but ρ and $D_{AB} \uparrow$ so k_c , E and $X \uparrow$

Particle size, d_p , affects k_c and a_c (not u if voidage remains the same)

$$k_c \propto \frac{1}{d_p^{1/2}} \quad \text{from T-K correlation}$$

$$a_c \propto \frac{1}{d_p}$$

$$\text{Hence } E \propto \frac{1}{d_p^{3/2}}$$

If $d_p \uparrow$ then E and $X \downarrow$

Problem P11-7a

Mesh, gas phase

$$\text{Mol balance : } \frac{dFa}{dV} = -k_c \cdot a_c \cdot C_a \qquad Fa_0 \frac{dX}{dV} = k_c \cdot a_c \cdot C_a$$

Stoichiometry : constant T , P

$$C_a = C_{a0} \cdot \frac{(1-X)}{(1+\epsilon \cdot X)} \qquad \epsilon = y_{a0} \cdot \delta$$

P11-7 cont'd

$$\text{voidage}, \epsilon = 1 - \pi \cdot L \cdot \frac{N^2 d}{4} = 1 - \pi \cdot \left[\frac{1}{250^2} + \left(\frac{0.044}{25.4} \right)^2 \right]^{1/2} \cdot 250^2 \cdot \frac{0.044}{25.4 \times 4} = 0.63$$

At STP (273 K, 1 atm) : $22.4 \text{ dm}^3 - 1 \text{ mol gas}$

$$\text{Assume ideal gas law : } V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{1 \times 22.4 \times 500}{2 \times 273} = 20.5 \text{ dm}^3 / \text{mol}$$

Total molar flowrate, $F_o = 8.44 \times 10 = 84.4 \text{ mol/min}$

$$u_o = 20.5 F_o = 20.5 \times 84.4 = 1731 \text{ dm}^3 / \text{min} = 1731 \text{e}3 \text{ cm}^3 / \text{min}$$

$$A_c = \frac{\pi \cdot d_{\text{mesh}}^2}{4} = \frac{\pi \cdot 10^2}{4} = 78.53 \text{ cm}^2$$

$$u = \frac{u_o}{A_c} = \frac{1731 \text{e}3}{78.53 \times 60} = 367.4 \text{ cm/s}$$

$$Re = \frac{1.387 \cdot \frac{3.67}{0.63} \cdot 0.044 \text{e} - 3}{2.7 \text{e} - 5} = 13.17$$

$$Sc = \left(\frac{\mu}{\rho \cdot D_{ab}} \right)$$

$$D_{\text{NH}_3, \text{air}} (295 \text{ K, 1 atm}) = 0.247 \text{ cm}^2 / \text{s}$$

$$D_{\text{NH}_3, \text{air}} (500 \text{ K, 2 atm}) = 0.247 \cdot \frac{1}{2} \cdot \left(\frac{500}{295} \right)^{1.75} = 0.311 \text{ cm}^2 / \text{s}$$

$$Sc = \left(\frac{2.7 \text{e} - 5}{1.387 \times 0.311 \text{e} - 4} \right) = 0.626$$

$$Sh = Sc^{1/3} \cdot Re \cdot J_D = \frac{kc \cdot d_w}{D_{ab}}$$

$$kc = \frac{0.311}{0.0044} \cdot 0.626^{1/3} \cdot 13.17 \cdot \frac{0.94}{13.17^{0.717}} = 118 \text{ cm/s}$$

11-16

P11-7 cont'd

For 1 mol NH_3

$$Nr = Na + Nb = 1 + 1.25 \frac{J}{4} \cdot \frac{1}{0.21} = 8.44$$

$$y_{A0} = \frac{1 - 0.118}{8.44}$$

$$\epsilon = 0.118 \times 0.25 = 0.0295$$

$$C_{A0} = y_{A0} \frac{P}{RT} = \frac{0.118 \times 2}{0.0821 \times 500 \text{ K}} = 0.00575$$

$$F_{A0} = \frac{10}{60} = 0.167 \text{ mol/min}$$

a_s = total screen surface area per total volume of one screen

$$= \pi \cdot L \cdot N^2 = \pi \cdot \left[\frac{1}{N^2} + d_w^2 \right]^{1/2} N^2 \quad N = \text{mesh size} = 250$$

$$= \pi \cdot \left[\frac{1}{250^2} + \left(\frac{0.044}{25.4} \right)^2 \right]^{1/2} 250^2 = 855 \text{ inch}^{-1} = 337 \text{ cm}^{-1}$$

Using Colburn J factor for k_c :

$$J_0 = \frac{Sh}{Sc^{1/3} Re} = \frac{0.94}{Re^{0.717}} \quad \text{for mesh}$$

$$Re = \frac{\rho \cdot u_i \cdot d_w}{\mu} \quad \text{but } u_i \text{ is the actual velocity in the mesh}$$

$$\text{and } u_i = \frac{u}{\phi} \quad \text{where } u \text{ is the superficial velocity}$$

$$\text{Assume } \rho (\text{air, 500 K, 2 atm}) = 1.387 \text{ kg/m}^3$$

$$\mu (\text{air, 500 K, 2 atm}) = 2.7 \text{ e-5 kg/m.s}$$

ChemCAD III physical properties database

P11-7 cont'd

Substituting into the mol balance:

$$\begin{aligned}\frac{dX}{dV} &= k_c a_s \frac{1-X}{(1+0.03X)} \\ &= 118 \times 337 \frac{0.00575e-3}{0.167} \frac{(1-X)}{(1+0.03X)} \\ &= 1.37 \frac{(1-X)}{(1+0.03X)}\end{aligned}$$

where

$$V_{\text{screen}} = \frac{\pi d_{\text{screen}}^2}{4} 2d_w = \frac{\pi \times 10^2 \times 2 \times 0.0044}{4} = 0.69 \text{ cm}^3$$

POLYMATH

Problem P11-7b

Equations:

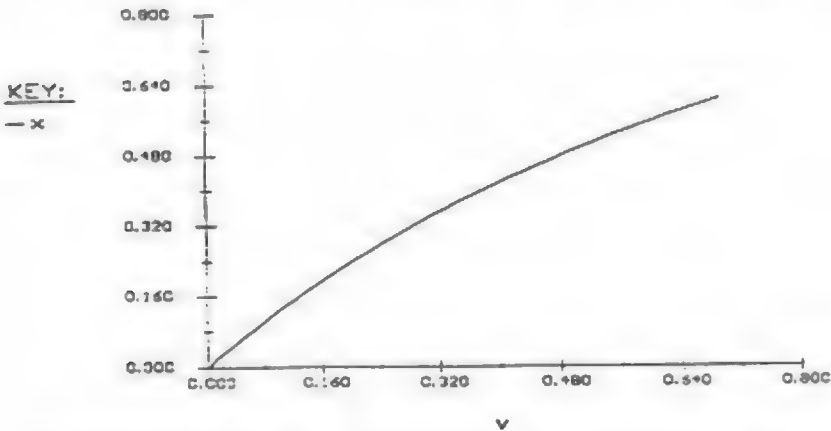
$$d(x)/d(v) = 1.37 \cdot (1-x) / (1 + (.03 \cdot x))$$

$$v_0 = 0, \quad v_f = 0.69$$

Initial value

0

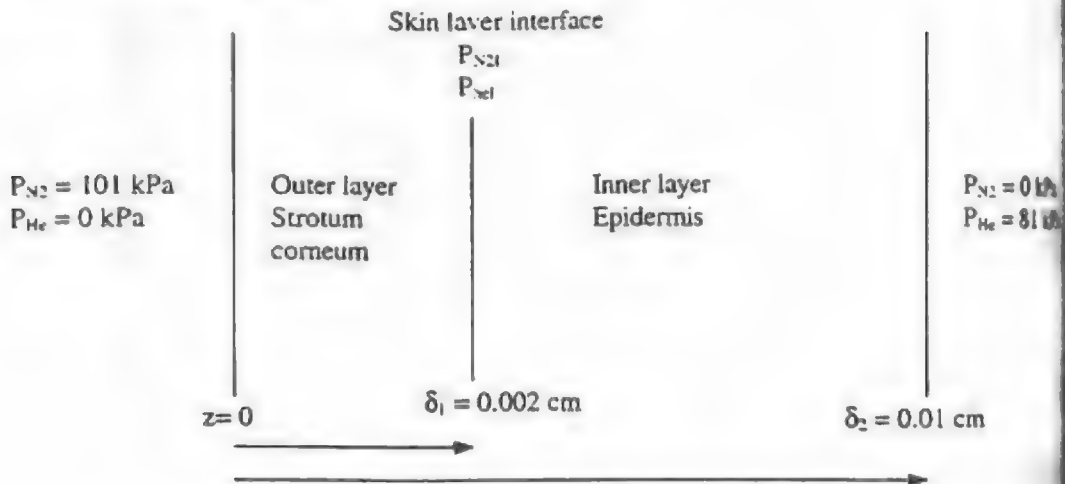
<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
v	0	0.69	0	0.69
x	0	0.607596	0	0.607596



The results show that with a single screen, the final conversion is 60.7 % and is just sufficient for the requirement.

Problem P11-8c

Diffusion in adjacent skin layers



Assuming dilute solution and constant total concentration in both layers gives:

$$\frac{d^2 C_A}{dz^2} = 0$$

$$\frac{d C_A}{dz} = K_1$$

$$C_A = K_1 \cdot z + K_2$$

for each diffusing component in each layer.

N_2 : Outer layer : boundary conditions $z = 0, C_A = C_{A0}$
 $z = \delta_1, C_A = C_{A1}$

$$K_1 = \frac{C_{A1} - C_{A0}}{\delta_1} \quad K_2 = C_{A0}$$

Profile $C_A = C_{A0} - (C_{A0} - C_{A1}) \cdot \frac{z}{\delta_1}$

Inner layer : boundary conditions $z = \delta_1, C_A = C_{A1}$
 $z = \delta_2, C_A = 0$

$$K_1 = -\frac{C_{A1}}{\delta_2 - \delta_1} \quad K_2 = \frac{C_{A1} \cdot \delta_2}{\delta_2 - \delta_1}$$

Profile $C_A = C_{A1} \cdot \left(\frac{\delta_2 - z}{\delta_2 - \delta_1} \right)$

P11-8 cont'd

Total partial pressure profiles

Outer skin layer :
$$P_A + P_B = P_{AO} - (P_{AO} - P_{Ai}) \frac{z}{\delta_i} + P_{Bi} \frac{z}{\delta_i}$$

$$= 1010 - (1010 - 1008) \frac{z}{0.002} + 10 \frac{z}{0.002}$$

$$= 1010 - 1000 \cdot z + 5000 \cdot z$$

$$= 1010 + 4000 \cdot z$$

Inner skin layer :

$$P_A + P_B = P_{Ai} \left(\frac{\delta_i - z}{\delta_i - \delta_o} \right) + P_{Bo} - (P_{Bo} - P_{Bi}) \left(\frac{\delta_i - z}{\delta_i - \delta_o} \right)$$

$$= 1008 \left(\frac{0.01 - z}{0.01 - 0.002} \right) + 810 - (810 - 10) \left(\frac{0.01 - z}{0.01 - 0.002} \right)$$

$$= 810 + 126000(0.01 - z) - 100000(0.01 - z)$$

$$= 810 + 26000(0.01 - z)$$

Check : At interface ($z = 0.002$ cm) : *outerlayer = innerlayer*

$$P_A + P_B = P_A + P_B$$

$$1010 + 4000 \cdot z = 810 + 26000(0.01 - z)$$

$$1018 = 1018 \quad \text{correct!}$$

Plot these two profiles across the skin from $z = 0$ to $z = 0.01$ cm

P11-8 cont'd

He : Inner layer : boundary conditions $z = \delta_1, C_B = C_{B1}$
 $z = \delta_2, C_B = C_{B0}$

$$K_1 = \frac{C_{B0} - C_{B1}}{\delta_2 - \delta_1} \quad K_2 = C_{B0} - \left(\frac{C_{B0} - C_{B1}}{\delta_2 - \delta_1} \right) \cdot \delta_2$$

Profile $C_B = C_{B0} - (C_{B0} - C_{B1}) \left(\frac{\delta_2 - z}{\delta_2 - \delta_1} \right)$

Outer layer : boundary conditions $z = \delta_1, C_B = C_{B1}$
 $z = 0, C_B = 0$

$$K_2 = 0 \quad K_1 = \frac{C_{B1}}{\delta_1}$$

Profile $C_B = C_{B1} \left(\frac{z}{\delta_1} \right)$

Total concentration profiles :

Outer skin layer : $C_A + C_B = C_{A0} - (C_{A0} - C_{A1}) \cdot \frac{z}{\delta_1} + C_{B1} \frac{z}{\delta_1}$

Inner skin layer : $C_A + C_B = C_{A1} \left(\frac{\delta_2 - z}{\delta_2 - \delta_1} \right) + C_{B0} - (C_{B0} - C_{B1}) \left(\frac{\delta_2 - z}{\delta_2 - \delta_1} \right)$

Evaluation of C_{A1} and C_{B1} :

N_2 : Outer layer : $W_{A1} = \frac{D_{1N2}}{\delta_1} [C_{A0} - C_{A1}]$

Inner layer : $W_{A2} = \frac{D_{2N2}}{\delta_2 - \delta_1} [C_{A1} - 0]$

Assume that flux in inner layer = flux in outer layer i.e. $W_{A1} = W_{A2}$

$$\frac{W_A}{\frac{D_{1N2}}{\delta_1}} = [C_{A0} - C_{A1}] \quad \frac{W_A}{\frac{D_{2N2}}{\delta_2 - \delta_1}} = [C_{A1} - 0]$$

P11-8 cont'd

$$W_A \left[\frac{1}{\frac{D_{1,N_2}}{\delta_1}} + \frac{1}{\frac{D_{2,N_2}}{\delta_2 - \delta_1}} \right] = C_{A0}$$

Conversion of kPa to kg/cm²s²

$$101 \text{ kPa} = 101000 \text{ Pa} = 101000 \text{ kg/ms}^2 = 1010 \text{ kg/cms}^2 \therefore 1 \text{ kPa} = 10 \text{ kg/cms}^2$$

$$W_A = \frac{C_{A0}}{\left[\frac{1}{\frac{D_{1,He}}{\delta_1}} + \frac{1}{\frac{D_{2,He}}{\delta_2 - \delta_1}} \right]} = \frac{810}{\left[\frac{1}{\frac{10 \cdot 10^{-5}}{0.002}} + \frac{1}{\frac{50 \cdot 10^{-7}}{0.008}} \right]} = 50 \cdot 10^{-2} \frac{\text{kg}}{\text{cm}^2 \text{s}^2}$$

He : Outer layer : $W_B = \frac{D_{1,He}}{\delta_2} [C_{B1} - 0]$

Inner layer : $W_B = \frac{D_{2,He}}{\delta_2 - \delta_1} [C_{B0} - C_{B1}]$

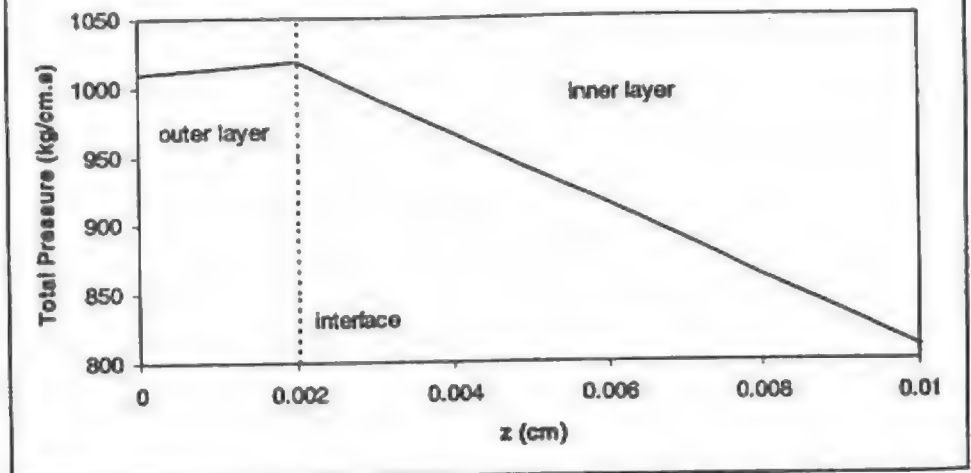
$$W_B \left[\frac{1}{\frac{D_{1,He}}{\delta_1}} + \frac{1}{\frac{D_{2,He}}{\delta_2 - \delta_1}} \right] = C_{B0}$$

$$W_B = \frac{C_{B0}}{\left[\frac{1}{\frac{D_{1,He}}{\delta_1}} + \frac{1}{\frac{D_{2,He}}{\delta_2 - \delta_1}} \right]} = \frac{81 \cdot 10}{\left[\frac{1}{\frac{10e-5}{0.002}} + \frac{1}{\frac{5 \cdot 10e-7}{0.008}} \right]} = 5 \cdot 10e-2 \text{ kg/cm}^2 \text{s}$$

Hence : $P_{A1} = \frac{W_A}{\frac{D_{1,N_2}}{\delta_2 - \delta_1}} = \frac{1.89 \cdot 10e-2}{\frac{1.5 \cdot 10e-7}{0.008}} = 1008 \text{ kg/cm}^2 \text{s}^2$

$$P_{B1} = \frac{W_B}{\frac{D_{2,He}}{\delta_1}} = \frac{5 \cdot 10e-2}{\frac{10e-5}{0.002}} = 10 \text{ kg/cm}^2 \text{s}^2$$

Pressure Profile of skin layers



The maximum sum of partial pressures occurs at the skin layer interface

$$z = 0.002 \text{ cm} \quad P_{\text{Total}} = 1018 \text{ kg/cm.s}^2$$

$$P_{\text{sat}} = 101 \text{ kPa} = 1010 \text{ kg/cm.s}^2 < P_{\text{Total}} = 1018 \text{ kg/cm.s}^2$$

Hence the maximum sum of the partial pressures is slightly greater than the saturation partial pressure and so gas will form bubbles at the skin layer interface causing blisters.

Problem P11-9_A

Dissolution of monodisperse solid particles in excess solvent.

$$D_i - D + \frac{1}{2D^*} (D_i^3 - D^3) = \alpha \cdot t$$

Define conversion in terms of volume dissolved :

$$X = \frac{\frac{\rho \cdot \pi}{6} (D_i^3 - D^3)}{\frac{\rho \cdot \pi}{6} D_i^3}$$

gives $D = D_i (1 - X)^{1/3}$

P11-9 cont'd

Substituting for D :
$$\underbrace{Di - Di(1 - X)^{1/3}}_{\text{term 1}} + \underbrace{\frac{1}{2D^*}(Di^2 - [Di(1 - X)^{1/3}]^2)}_{\text{term 2}} = \alpha \cdot t$$

Surface reaction controls : D^* is large, term 2 is small of term 1

$$Di - Di(1 - X)^{1/3} = \alpha \cdot t$$

$$1 - (1 - X)^{1/3} = \frac{\alpha \cdot t}{Di}$$

Mass transfer controls : D^* is small, term 1 is small of term 2

$$\frac{1}{2D^*}(Di^2 - [Di(1 - X)^{1/3}]^2) = \alpha \cdot t$$

$$\frac{Di}{2D^*}(1 - (1 - X)^{2/3}) = \frac{\alpha \cdot t}{Di}$$

Both regimes apparent : Term 1 and term 2 apply

$$[1 - (1 - X)^{1/3}] + \left[\frac{Di}{2D^*}(1 - (1 - X)^{2/3}) \right] = \frac{\alpha \cdot t}{Di}$$

Problem P11-10c

Part (a)

Mass transfer limited $-W_A = k_C \cdot C_{AO}$ A in excess, $C_A = C_{AO}$

The reaction rate is equal to the mass transfer rate $-r_A'' = k_r \cdot C_A = k_C \cdot C_{AO}$

For small particles and negligible shear stress :

$$k_C = \frac{2 \cdot De}{D}$$

$$-r_A'' = \frac{2 \cdot De}{D} \cdot C_{AO}$$

P11-10 cont'd

Mol balance on solids :

$$r_{B,i}'' \pi D^2 = \frac{d \left(\frac{\rho \pi D^3}{6} \right)}{dt} = \frac{\rho \pi D^2}{6} \frac{dD}{dt}$$

For 1 mole A dissolving 1 mole B then $-r_{A,i}'' = -r_{B,i}'' = k_c \cdot C_{A0}$ as $C_{A,i}$ is undefined

$$\frac{dD}{dt} = - \left[\frac{2 \cdot (-r_{A,i}'')}{\rho} \right] = - \frac{4 \cdot De \cdot C_{A0}}{\rho \cdot D}$$

Boundary conditions, $t = 0$, $D = D_i$

$$\int_{D_i}^D (D) dD = - \frac{4 \cdot De \cdot C_{A0}}{\rho} \int_0^t dt$$

$$\frac{D^2 - D_i^2}{2} = - \frac{4 \cdot De \cdot C_{A0} \cdot t}{\rho}$$

$$D = \left[D_i^2 - \frac{8 \cdot De \cdot C_{A0} \cdot t}{\rho} \right]^{1/2}$$

Time for dissolution, t_c , at $D = 0$, and assuming particle density, $\rho = 2000 \text{ kg/m}^3$

$$t_c = \frac{\rho \cdot D_i^2}{8 \cdot De \cdot C_{A0}} = \frac{2000 \times (10e-5)^2}{8 \times (10e-10) \times (2000)} = 0.125 \text{ s}$$

i.e. virtually instantaneous dissolution

Part (b)

Surface reaction limited $-r_{A,i}'' = k_r \cdot C_{A0}$

Mass transfer effects are not important when the surface reaction rate is limiting.

Mol balance on solids :

$$r_{B,i}'' \cdot \pi \cdot D^2 = \frac{d \left(\frac{\rho \cdot \pi \cdot D^3}{6} \right)}{dt}$$

For 1 mole A dissolving 1 mole B then $-r_{A,i}'' = -r_{B,i}''$

P11-10cont'd

$$\frac{dD}{dt} = - \left[\frac{2(-r_A'')}{\rho} \right] = - \frac{2}{5} k_r C_{A0}$$

Boundary conditions, $t = 0$, $D = D_i$

$$\int_{D_i}^0 dD = - \frac{2 k_r C_{A0}}{\rho} \int_0^t dt$$

$$D - D_i = - \frac{2 k_r C_{A0} t}{\rho}$$

$$D = D_i - \frac{2 k_r C_{A0} t}{\rho}$$

Time for dissolution, t_c , at $D = 0$, and assuming particle density, $\rho = 2000 \text{ kg/m}^3$

$$t_c = \frac{\rho \cdot D_i}{2 k_r C_{A0}} = \frac{2000 \times (10e-5)}{2 \times (10e-10) \times (2000)} = 5 \times 10^6 \text{ s}$$

a very long time.

Part (c)

At $t = 0$, total moles A in tank = $0.1 \times 100 = 10 \text{ mol A}$

i.e. there is just enough mols of A to completely dissolve all of B in a well mixed tank.

Acid not in excess and dissolution is mass transfer limited ($C_{As} \neq 0$ and $C_A \neq C_{A0}$)

$$W_{Ar} = k_c(C_A - C_{As}) = -r_A'' = k_r C_{As} \quad \text{assume zero order in B}$$

$$W_{Ar} = k_c(C_A - C_{As}) = -r_A'' = \frac{k_c k_r}{k_c + k_r} C_A \quad \text{and} \quad k_c = \frac{2 \cdot De}{D}$$

$$-r_A'' = \frac{k_r}{1 + \frac{D}{D^*}} C_A \quad \text{where} \quad D^* = \frac{2 \cdot De}{k_r}$$

Mol balance on solids :

$$r_{As}'' \cdot \pi \cdot D^2 = - \frac{d \left(\frac{\rho \cdot \pi \cdot D^3}{6} \right)}{dt}$$

For 1 mole A dissolving 1 mole B then $-r_{As}'' = -r_{Bs}''$

$$\frac{dD}{dt} = - \left[\frac{2 \cdot (-r_{As}'')}{\rho} \right] = - \frac{2 \cdot kr \cdot C_A}{\rho} \left(\frac{1}{1 + \frac{D}{D^*}} \right)$$

$$\frac{dD}{dt} = -\alpha \cdot \left(\frac{1}{1 + \frac{D}{D^*}} \right) \quad \text{where } \alpha = \frac{2 \cdot kr \cdot C_A}{\rho}$$

Boundary conditions. $t = 0$, $D = D_i$

$$D_i - D + \frac{1}{2 \cdot D^*} \cdot (D_i^2 - D^2) = \alpha \cdot t$$

As a function of radius :

$$\frac{2r^2}{D} - 2r + \alpha - 2ri - \frac{2ri^2}{D^*} = 0$$

$$r^2 + D^* \cdot r + \left[\frac{D^* \cdot \alpha \cdot t}{2} - D^* \cdot ri - ri^2 \right] = 0$$

Using the quadratic solver : $r = \frac{-b \pm \sqrt{b^2 - 4 \cdot a \cdot c}}{2 \cdot a}$

$$r = \frac{-D^* \pm \sqrt{(D^*)^2 - 4 \left(\frac{D^* \alpha t}{2} - D^* ri - ri^2 \right)}}{2}$$

Time for complete dissolution, t_c , at $r = 0$:

$$t_c = \frac{1}{\alpha} \left[D_i + \frac{D_i^2}{2 \cdot D^*} \right]$$

P11-10cont'd

assume $\rho = 2000 \text{ kg/m}^3$ and $\alpha = \frac{2 \cdot kr \cdot C_A}{\rho} = \frac{2 \times (10e-18) \times (0.1e3)}{2000} = 10e-19$

$$D^* = \frac{2 \cdot De}{kr} = \frac{2 \times (10e-10)}{10e-18} = 2 \times 10e8$$

gives $t_c = \frac{1}{10e-19} \left[(10e-5) + \frac{(10e-5)^2}{2 \times (2 \times 10e-8)} \right] = 10e14 \text{ s}$
again a very long time.

Part (d)

$$t_c = \frac{\rho}{2 \cdot kr \cdot C_A} \left[Di + \frac{Di^2}{2 \cdot D^*} \right]$$

To reduce t_c , increase C_A and / or decrease Di .

To increase t_c , decrease C_A and / or increase Di .

Problem P11-11a

Irreversible, gas-phase, adiabatic, no pressure drop, packed bed.

Part (a) Isothermal

Mol balance : $F_{A0} \cdot \frac{dX}{dW} = -r_A$ mol/gcat s

where $F_{A0} = C_{A0} \cdot v_0 = 10e-3 \times 10e4 = 10 \text{ mol/cm}^3$

Rate law : $-r_{Ax} = k' \cdot C_{Ax}$ But C_{Ax} is unknown.

Assume reaction rate is mass transfer limited.

$$W_A = kc \cdot (C_A - C_{Ax}) = k' \cdot C_{Ax}$$

P11-11cont'd

$$C_A = \frac{k_c \cdot C_A}{k_c + k'}$$

$$-r_A = \frac{k' \cdot k_c \cdot C_A}{k_c + k'} \quad \frac{\text{cm}^3}{\text{s} \cdot \text{gcat}} \cdot \frac{\text{mol}}{\text{cm}^3}$$

where $k' = 0.01 \text{ cm}^3/\text{s} \cdot \text{gcat}$ at 300 K (constant - isothermal)

$$\text{Sh} = 100 \cdot \text{Re}^{1/2}$$

$$k_c = \frac{De}{dp} 100 \left(\frac{u \cdot dp}{v} \right)^{1/2} = \frac{10e-2}{0.1} 100 \left(\frac{10 \cdot 0.1}{0.02} \right)^{1/2} = 70.7 \text{ cm/s}$$

converting: $70.7 \times a_{\text{cat}} = 70.7 \times 60 = 4242 \text{ cm}^3/\text{s} \cdot \text{gcat}$

$$-r_A = \frac{0.01 \times 4242 \times C_A}{4242 + 0.01}$$

Stoichiometry:

gas-phase, constant pressure and temperature

$$C_A = C_{A0} \left(\frac{1-X}{1+\varepsilon \cdot X} \right)$$

where $\varepsilon = y_{A0} \delta = 0.5(1-1) = 0$

$$C_A = C_{A0}(1-X) \quad \text{and } C_{A0} = 1 \text{ mol/dm}^3 = 10e-3 \text{ mol/cm}^3$$

POLYMATH

Problem P11-11B part a

Equations:

$$d(x)/d(w) = -r_A/f_{A0}$$

$$k = 0.01$$

$$f_{A0} = 10$$

$$k_c = 4242$$

$$C_{A0} = 0.001$$

$$C_A = C_{A0}(1-X)$$

$$r_A = -(k \cdot k_c \cdot C_A) / (k + k_c)$$

$$w_0 = 0, \quad w_f = 1e+06$$

Initial value

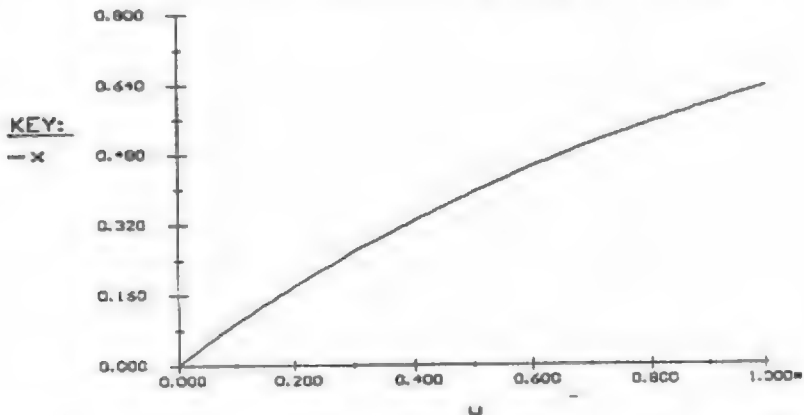
0

11-29

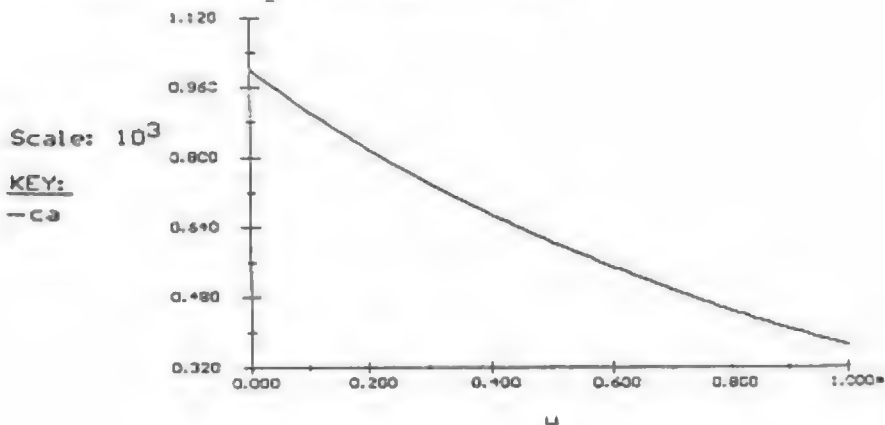
P11-11cont'd

Problem P11-11B part a

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	1e+06	0	1e+06
x	0	0.63212	0	0.63212
k	0.01	0.01	0.01	0.01
fao	10	10	10	10
kc	4242	4242	4242	4242
cao	0.001	0.001	0.001	0.001
ca	0.001	0.001	0.00036788	0.00036788
ra	-9.99998e-06	-3.67879e-06	-9.99998e-06	-3.67879e-06



For a conversion of $X = 60\%$, $W_{in} = 925 \text{ kg}$



11-30

P11-11cont'd

Part (b) Adiabatic operation

Mol balance and rate law as in Part (a)

$$\text{with } k(T) = 0.01 \exp \left[\frac{4000}{1.987} \left(\frac{1}{300} - \frac{1}{T} \right) \right]$$

Stoichiometry : $C_A = C_{A0} \left(\frac{1-X}{1+\epsilon_A X} \right) \frac{T_0}{T}$ where $\epsilon = 0$ and $T_0 = 300 \text{ K}$
 and $C_{A0} = 10 \text{e-3 mol/cm}^3$

Energy balance : $\frac{dF}{dt} = \frac{Q - W_s - \sum F_{i0} C_{pi} (T - T_{i0}) + F_{A0} X (-\Delta H_{RX}(T))}{\sum N_i C_{pi}} = 0$

$$\sum F_{i0} C_{pi} (T - T_{i0}) = [10 \times 25 (T - 300)] + [10 \times 75 (T - 750)]$$

$$= 1000 (T - 300)$$

$$- 1000 (T - 300) + 10 X (10000) = 0$$

POLYMATH

Problem P11-11B part b

Equations:

$$d(x)/d(w) = -ra/iao$$

$$k=0.01$$

$$iao=10$$

$$kc=4242$$

$$cao=0.001$$

$$To=300$$

$$T=(10 \times x \times 10000/1000) + To$$

$$ca=cao \cdot (1-x) \cdot (To/T)$$

$$ra=-(k \cdot kc \cdot ca)/(k+kc)$$

$$w_0 = 0, \quad w_f = 1.2 \text{e}+06$$

Initial value

0

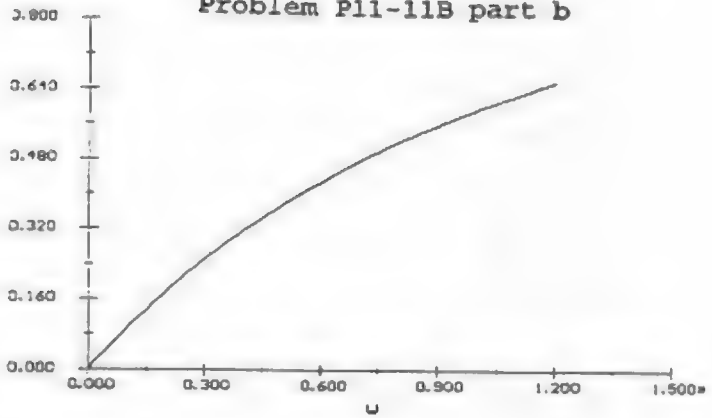
<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
w	0	1.2e+06	0	1.2e+06
x	0	0.654825	0	0.654825
k	0.01	0.01	0.01	0.01
iao	10	10	10	10
kc	4242	4242	4242	4242
cao	0.001	0.001	0.001	0.001
To	300	300	300	300
T	300	365.483	300	365.483
ca	0.001	0.001	0.000283331	0.000283331
ra	-9.99998e-06	-2.8333e-06	-9.99998e-06	-2.8333e-06

11-31

Problem P11-11B part b

KEY:

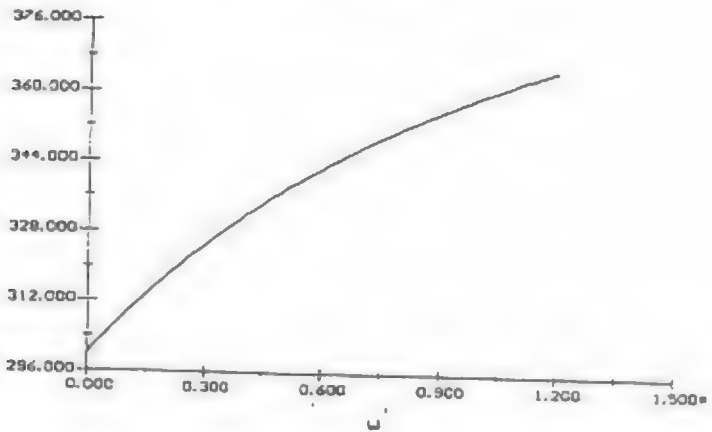
- x

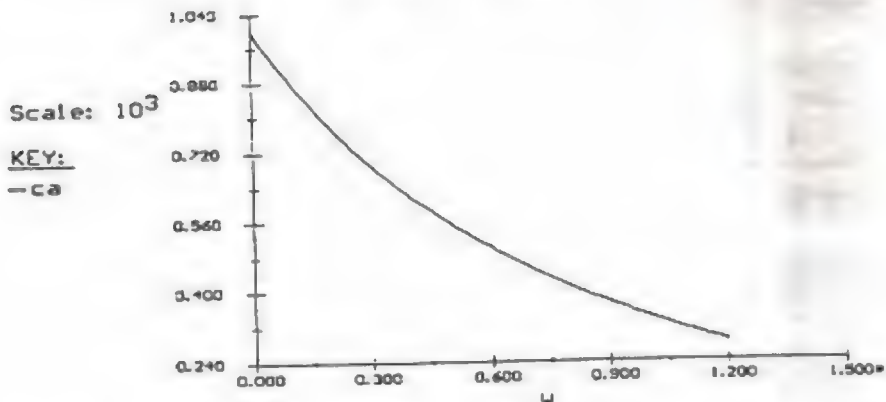


For a conversion of $X = 60\%$, $W_{cat} = 1020$ kg

KEY:

- T





Part (c)

It is possible to generalize that the addition of temperature variation in adiabatic operation does not affect the conversion, concentration profiles in form, but the numerical values are slightly different. Because the reaction is exothermic, isothermal operation enhances the conversion profile along the packed bed, so that for a given bed diameter less catalyst is required. It is clear that adiabatic operation inhibits conversion as heat is not removed from the system so more catalyst is needed for the required conversion. The removal of the heat generated in the reaction allows a reduction of 85 kg of catalyst in the bed. More detailed economics will indicate whether isothermal operation is worth it.

Problem P11-12c

Dissolution of pills.

Part (a)

Complete dissolution.

$$C_B = \frac{W_{\text{drug in blood}}}{W_{\text{body}}}$$

$$C_A = \frac{W_{\text{drug in stomach}}}{V_{\text{stomach}}}$$

$$\frac{dC_B}{dt} = k_A \cdot C_A \frac{V_{\text{stomach}}}{W_{\text{body}}} \quad \frac{\text{g drug}}{\text{g body min}}$$

Relate C_A to time :

Three pills, each with different thickness outer layers, the inner cores dissolving at different times (but at the same rate) to each other, will each contribute to C_A in the stomach.

Pill 1 : $D_2 = 5 \text{ mm}$, $D_1 = 3 \text{ mm}$

$$\text{Time for outer layer to dissolve } t_1 = \frac{0.0354 \cdot x(0.5^2 - 0.3^2)}{8 \cdot x(6 \times 10^{-4} - 4) \cdot x 1.0} = 1.18 \text{ min}$$

Pill 2 : $D_2 = 4 \text{ mm}$, $D_1 = 3 \text{ mm}$

$$\text{Time for outer layer to dissolve } t_1 = \frac{0.0354 \cdot x(0.4^2 - 0.3^2)}{8 \cdot x(6 \times 10^{-4} - 4) \cdot x 1.0} = 0.52 \text{ min}$$

Pill 3 : $D_2 = 3.5 \text{ mm}$, $D_1 = 3 \text{ mm}$

$$\text{Time for outer layer to dissolve } t_1 = \frac{0.0354 \cdot x(0.35^2 - 0.3^2)}{8 \cdot x(6 \times 10^{-4} - 4) \cdot x 1.0} = 0.24 \text{ min}$$

At $t = t_1$

mol balance on drug :

$$r_A'' \cdot \pi \cdot D_1^2 = \frac{dW_{\text{drug in stomach}}}{dt}$$

drug in stomach

$$\text{where } C_A = \frac{W_{\text{drug in stomach}}}{V}$$

and

$$r_A'' = k_c \cdot S_m \quad k_c S_m$$

$$\frac{dC_A}{dt} = \frac{k_c \cdot S_m \cdot \pi \cdot D^2}{V} = \frac{2 \cdot D_{AB} \cdot S_m \cdot \pi \cdot D^2}{D \cdot V}$$

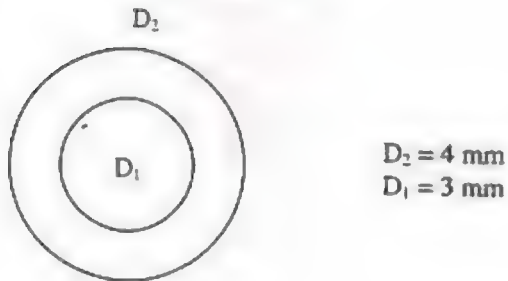
where W = mass of drug in stomach, g
 V = volume stomach fluid, cm^3

and boundary conditions :

$$t = t_1, C_A = 0$$

$$t = t_2, C_A = C_{A0} = W_0/V = 0.5/1200 = 4.17 \times 10^{-4} \text{ g/cm}^3$$

P11-12cont'd



Outer layer :

$$\text{Mol balance on outer layer : } 0 - 0 + r_A'' \cdot \pi \cdot D^2 = \frac{\left(\frac{1}{6} \cdot \pi \cdot D^3 \rho_c \right)}{dt}$$

and r_A'' rate of dissolution of outer layer = rate of mass transfer from pill surface W_A

$$W_A = k_c \cdot S_{out} = -r_A''$$

$$Sh = 2, \quad k_c = \frac{2 \cdot D_{AB}}{D}$$

$$\text{Assume density of outer layer} = \text{inner layer} = \frac{500 \times 10^{-6}}{\frac{\pi \cdot (0.3)^3}{6}} = 0.0354 \text{ kg/cm}^3$$

$$S_{out} = 1.0 \text{ kg/cm}^3$$

$$\frac{dD}{dt} = - \frac{2 \cdot (-r_A'')}{\rho} = - \frac{2 \times 2 \times D_{AB} \cdot S_{out}}{D \cdot \rho}$$

Boundary conditions :

$$t = 0, \quad D = D_2$$

$$t = t_1, \quad D = D_1$$

$$\frac{D_2^2 - D_1^2}{2} = \frac{2 \times 2 \cdot D_{AB} \cdot S_{out}}{\rho} \cdot t_1$$

where t_1 = time for outer layer to dissolve

$$t_1 = \frac{0.0354 \times (0.4^2 - 0.3^2)}{8 \times (6 \times 10^{-4}) \times 1.0} = 0.52 \text{ min}$$

P11-12cont'd

Inner core :

Boundary conditions :

$$t = 0, D = D_1$$

$$t = t_2, D = 0$$

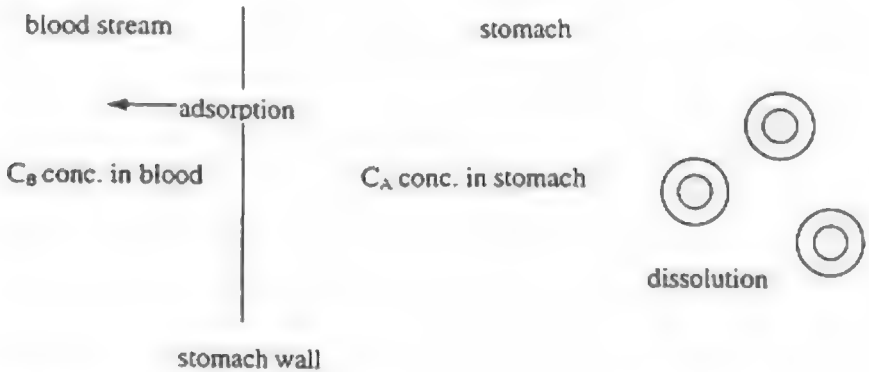
$$\frac{D_1^2}{2} = \frac{2 \times 2 \cdot D_{AB} \cdot S_m}{\rho} \cdot t_2$$

where t_2 = time for inner core to dissolve

$$t_2 = \frac{0.0354 \times 0.3^2}{8 \times (6 \times 10^{-4}) \times 0.4} = 1.66 \text{ min}$$

time for complete dissolution, $t_T = t_1 + t_2 = 0.52 + 1.66 = 2.18 \text{ min}$

Part (b)



Let rate of adsorption into bloodstream

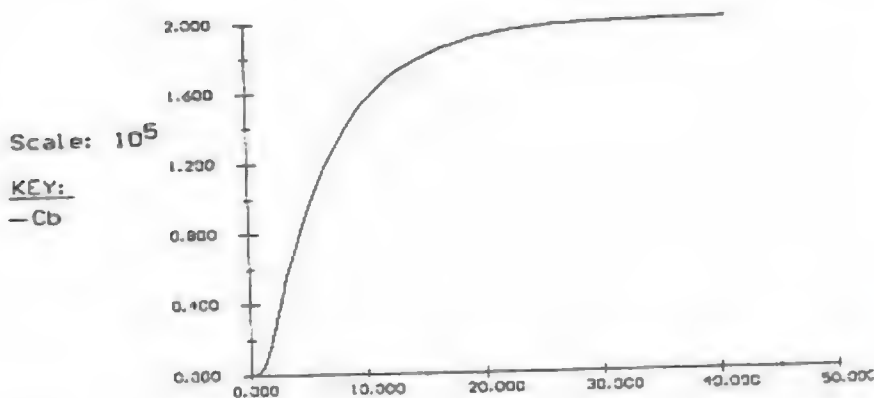
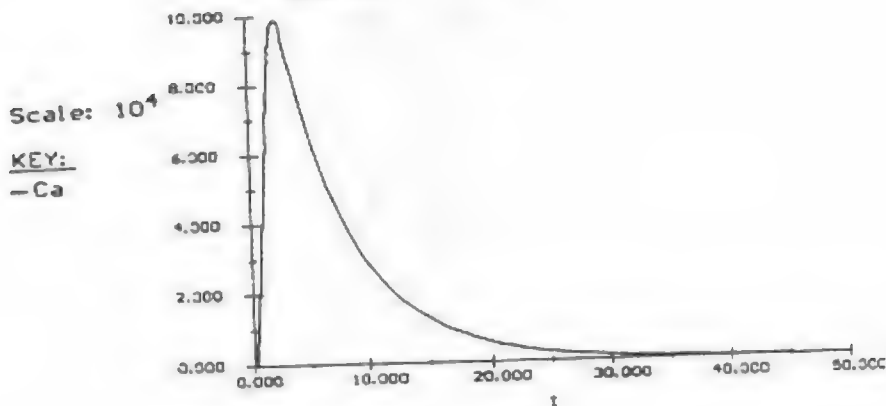
$$-r_A'' = k_A \cdot C_A$$

Relate concentration in stomach C_A , to concentration in blood C_B :

Mol balance on drug in bloodstream :

$$-r_A'' = \frac{dC_B}{dt}$$

$$\frac{dC_B}{dt} = k_A \cdot C_A$$



Part (c)

The graph of C_b against time shows how the drug concentration in the bloodstream initially varies with time and then becomes independent of time as all the drug initially in the stomach has absorbed into the blood (consumption of the drug within the bloodstream has not been modelled, unrealistic but no data). If a certain drug level is specified, and assuming a constant size of inner core (drug) and that the pills were to be taken simultaneously, then the way to achieve this would be to use pills of different outer layer thicknesses - to maintain an even stomach concentration and hence absorption rate over the whole period.

P11-12cont'd

$$\text{Relate } D \text{ with time : } \frac{dD}{dt} = -\frac{2 \cdot k_c \cdot S_m}{\rho} = -\frac{4 \cdot D_{AB} \cdot S_m}{D \cdot \rho}$$

$$\text{and boundary conditions : } \begin{aligned} t &= t_1, D = D_1 \\ t &= t_2, D = 0 \end{aligned}$$

Using logic to obtain the correct timing for the drug concentration profiles inside the stomach for each pill, the total profile is used in the relation with the concentration profile in the bloodstream.

P11-12C

Equations:

$$\begin{aligned} d(D1)/d(t) &= \text{if}(t > 0.24) \text{ then } (\text{if}(D1 > 0.00001) \text{ then } (-4 \cdot D_{AB} \cdot \sin / (D1 \cdot \rho)) \text{ else } (0)) \text{ else } (0) & \text{Initial value } 0.3 \\ d(Cb)/d(t) &= k_a \cdot C_a \cdot V / W_{body} & 0 \\ d(Ca1)/d(t) &= \text{if}(t > 0.24) \text{ then } (2 \cdot D_{AB} \cdot \sin \cdot 3.14 \cdot D1 / V) \text{ else } (0) & 0 \\ d(Ca2)/d(t) &= \text{if}(t > 0.52) \text{ then } (2 \cdot D_{AB} \cdot \sin \cdot 3.14 \cdot D2 / V) \text{ else } (0) & 0 \\ d(D2)/d(t) &= \text{if}(t > 0.52) \text{ then } (\text{if}(D2 > 0.00001) \text{ then } (-4 \cdot D_{AB} \cdot \sin / (D2 \cdot \rho)) \text{ else } (0)) \text{ else } (0) & 0.3 \\ d(Ca3)/d(t) &= \text{if}(t > 1.18) \text{ then } (2 \cdot D_{AB} \cdot \sin \cdot 3.14 \cdot D3 / V) \text{ else } (0) & 0 \\ d(D3)/d(t) &= \text{if}(t > 1.18) \text{ then } (\text{if}(D3 > 0.00001) \text{ then } (-4 \cdot D_{AB} \cdot \sin / (D3 \cdot \rho)) \text{ else } (0)) \text{ else } (0) & 0.3 \end{aligned}$$

$$D_{AB} = 0.0006$$

$$\sin = 400$$

$$\rho = 35.4$$

$$k_a = 0.166667$$

$$V = 1200$$

$$W_{body} = 75000$$

$$C_a = Ca1 + Ca2 + Ca3 - (Cb \cdot W_{body} / V)$$

$$t_0 = 0, \quad t_f = 45$$

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	45	0	45
D1	0.3	0.3	9.9965e-06	9.9965e-06
Cb	0	2.00164e-05	0	2.00164e-05
Ca1	0	0.000417376	0	0.000417376
Ca2	0	0.000417373	0	0.000417373
D2	0.3	0.3	9.99774e-06	9.99774e-06
Ca3	0	0.000417364	0	0.000417364
D3	0.3	0.3	9.99841e-06	9.99841e-06
Dab	0.0006	0.0006	0.0006	0.0006
Sin	400	400	400	400
rho	35.4	35.4	35.4	35.4
ka	0.166667	0.166667	0.166667	0.166667
V	1200	1200	1200	1200
Wbody	75000	75000	75000	75000
Ca	0	0.00099118	0	1.09044e-06

P11-12cont'd

Relate D with time : $\frac{dD}{dt} = -\frac{2 \cdot k_c \cdot S_{ia}}{\rho} = -\frac{4 \cdot D_{AB} \cdot S_{ia}}{D \cdot \rho}$

and boundary conditions : $t = t_1, D = D_1$
 $t = t_2, D = 0$

Using logic to obtain the correct timing for the drug concentration profiles inside the stomach for each pill, the total profile is used in the relation with the concentration profile in the bloodstream.

P11-12C

<u>Equations:</u>	<u>Initial value</u>
$d(D1)/d(t) = \text{if}(t > 0.24) \text{ then } (\text{if}(D1 > 0.00001) \text{ then } (-4 \cdot Dab \cdot \sin / ($	0.3
$D1 \cdot \rho)) \text{ else } (0)) \text{ else } (0)$	
$d(Cb)/d(t) = ka \cdot Ca \cdot V / Wbody$	0
$d(Ca1)/d(t) = \text{if}(t > 0.24) \text{ then } (2 \cdot Dab \cdot \sin \cdot 3.14 \cdot D1 / V) \text{ else } (0)$	0
$d(Ca2)/d(t) = \text{if}(t > 0.52) \text{ then } (2 \cdot Dab \cdot \sin \cdot 3.14 \cdot D2 / V) \text{ else } (0)$	0
$d(D2)/d(t) = \text{if}(t > 0.52) \text{ then } (\text{if}(D2 > 0.00001) \text{ then } (-4 \cdot Dab \cdot \sin / ($	0.3
$D2 \cdot \rho)) \text{ else } (0)) \text{ else } (0)$	
$d(Ca3)/d(t) = \text{if}(t > 1.18) \text{ then } (2 \cdot Dab \cdot \sin \cdot 3.14 \cdot D3 / V) \text{ else } (0)$	0
$d(D3)/d(t) = \text{if}(t > 1.18) \text{ then } (\text{if}(D3 > 0.00001) \text{ then } (-4 \cdot Dab \cdot \sin / ($	0.3
$D3 \cdot \rho)) \text{ else } (0)) \text{ else } (0)$	

$Dab = 0.0006$
 $Sin = 400$
 $\rho = 35.4$
 $ka = 0.166667$
 $V = 1200$
 $Wbody = 75000$
 $Ca = Ca1 + Ca2 + Ca3 - (Cb \cdot Wbody / V)$

$t_0 = 0, \quad t_f = 45$

<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
t	0	45	0	45
D1	0.3	0.3	9.9965e-06	9.9965e-06
Cb	0	2.00164e-05	0	2.00164e-05
Ca1	0	0.000417376	0	0.000417376
Ca2	0	0.000417373	0	0.000417373
D2	0.3	0.3	9.99774e-06	9.99774e-06
Ca3	0	0.000417364	0	0.000417364
D3	0.3	0.3	9.99841e-06	9.99841e-06
Dab	0.0006	0.0006	0.0006	0.0006
Sin	400	400	400	400
rho	35.4	35.4	35.4	35.4
ka	0.166667	0.166667	0.166667	0.166667
V	1200	1200	1200	1200
Wbody	75000	75000	75000	75000
Ca	0	0.00099118	0	1.09044e-06

P11-12cont'd

Part (d)

To maintain constant drug level by maintaining a constant stomach concentration, time needs to be allowed for the dissolution of the outer layer. for a given period of say 3 hours, a size distribution of outer layers is needed, with thin layers for initial response and thicker layers for delayed response. This distribution would be back calculated given the necessary stomach concentration for the required bloodstream concentration accounting for bloodstream drug consumption. Optimization of the stomach concentration will indicate the times at which complete dissolution of the outer layer of the 'next' pill is required to maintain this level. The range of pill sizes depends on the number of pills which can be reasonably consumed in one sitting, the period for effect and the limits of practical pill size.

Problem P11-13_n

Part (a)

A possible reason is a reduction in the conversion of hydrazine in the packed bed.

$$X = 1 - \exp\left[-\frac{kc \cdot a_c \cdot L}{u}\right]$$

The two routes of investigation are :

- 1) Possible sabotage of the hydrazine / helium
- 2) Possible sabotage of the packed bed

Three logical questions may be :

- 1) What was the size of the packing particles used ? (affects kc and a_c)
- 2) What was the bed porosity ? (affects kc)
- 3) What was the composition of the fuel mixture ? (affects D_{AB})

Part (b)

Thoenes and Kramer's correlation $Sh' = (Re')^{1/2} (Sc)^{1/3}$

P11-13cont'd

$$k_c = \frac{D_{AB}}{d_p} \cdot \frac{(1-\phi)}{\phi} \cdot \gamma \cdot \left[\frac{\rho \cdot u \cdot d_p}{\mu \cdot (1-\phi) \cdot \gamma} \right]^{1/2} \left[\frac{\mu}{\rho \cdot D_{AB}} \right]^{1/3}$$

$$k_c = \frac{D_{AB}^{2/3}}{d_p} \cdot \frac{(1-\phi)^{1/2}}{\phi} \cdot \gamma^{1/2} \cdot \left[\frac{\rho \cdot u \cdot d_p}{\mu} \right]^{1/2} \left[\frac{\mu}{\rho} \right]^{1/3}$$

$$\text{but } \gamma = \frac{2 \cdot r \cdot \pi \cdot L_p + 2 \cdot \pi \cdot r^2}{\pi \cdot d_p^2}$$

$$k_c = 2^{1/2} \frac{D_{AB}^{2/3}}{d_p^{1/2}} \cdot \frac{(1-\phi)^{1/2}}{\phi} \left[\frac{r \cdot L_p + r^2}{d_p^2} \right]^{1/2} \left[\frac{\rho}{\mu} \right]^{1/6} u^{1/2}$$

$$k_c = 2^{1/2} \frac{D_{AB}^{2/3}}{d_p^{3/2}} \cdot \frac{(1-\phi)^{1/2}}{\phi} [r \cdot L_p + r^2]^{1/2} \left[\frac{\rho}{\mu} \right]^{1/6} u^{1/2}$$

$$D_{AB}(T) = D_{AB}(298 \text{ K}) \left(\frac{T}{298} \right)^{1.75}$$

$$a_c = \frac{6 \cdot (1-\phi)}{d_p}$$

A reduction in the conversion X would mean that not all the fuel mixture decomposed and hence there would not be the required amount of energy or thrust released, causing the crash.

$$X = 1 - \exp \left[- \frac{k_c \cdot a_c \cdot L}{u} \right]$$

$$\text{and } \frac{k_c \cdot a_c \cdot L}{u} = 6 \cdot (2)^{1/2} \frac{D_{AB}^{2/3}}{d_p^{5/2}} \cdot \frac{(1-\phi)^{3/2}}{\phi} [r \cdot L_p + r^2]^{1/2} \left[\frac{\rho}{\mu} \right]^{1/6} \frac{L}{u^{1/2}}$$

Term 1

P11-13cont'd

If term 1 decreases then X also decreases.

Possible reasons for the reduction in X could be :

- Increase in volume-average particle diameter, reduction in cylindrical radius and/or length of particle.

d_p particularly has a large influence on X : $\frac{kc \cdot a_c \cdot L}{u} \propto \frac{1}{d_p^{3/2}}$

- Increase in porosity of bed, ϕ (due to change in packing shape), small effect on X.
- Change in fuel properties : decrease in ρ
increase in μ

small impact on X $\frac{kc \cdot a_c \cdot L}{u} \propto \left[\frac{\rho}{\mu} \right]^{1/6}$

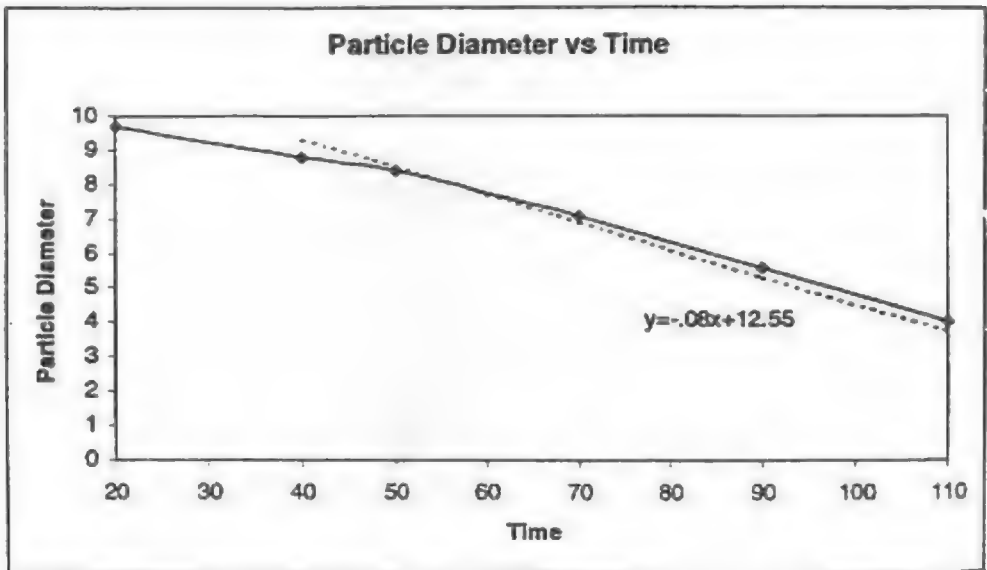
- Change in fuel composition :
 - probably insignificant effect on fluid properties
 - increase in % hydrazine - diffusivity, D_{AB} possibly decreased
 - decrease in % hydrazine - less energy release
- Decrease in gas velocity, u (pump malfunction, wrong storage pressure)
 $\frac{kc \cdot a_c \cdot L}{u} \propto \frac{1}{u^{1/2}}$ if $u > 1$ m/s then X increases but if $u < 1$ then X decreases.

- Reduction in bed length, L $\frac{kc \cdot a_c \cdot L}{u} \propto L$
an unlikely cause unless no packing is used.

- Wrong catalyst used in bed.
- Catalyst had become poisoned./deactivated - slower surface reaction may become limiting.
- Isothermal operation not achieved - failure of cooling system, may have caused a structural fault.
- Non-uniform physical properties of the packing inside the bed - plugging, channelling etc. will create hot/cold spots and uneven distribution of thrust.

Problem P11-14g

The plot of the data is shown below.



Initially the rate of incineration of the droplet in terms of diameter, is non-linear, but apparently becomes linear after ~ 50 time units. The linear form of the data indicates that the diameter is directly proportional to time and the rate of decrease in diameter is constant and hence not a function of diameter. This relationship should make it easier to estimate the required incineration time for complete destruction (zero diameter).

Assuming that rate of diameter decrease continues at the linear rate until complete destruction (at time t_d and hence complete decomposition of the POHC's, the equation for the linear relation indicates $t_d \sim 160$ units.

Problem 11-15g

Mol balance on layer of earth control volume:

$$F_{A1} - F_{A1+\Delta z} = A_c \Delta z \frac{dC_A}{dt} \quad \text{but } F_A = A_c W_A$$

$$\frac{A_c W_{A1} - A_c W_{A1+\Delta z}}{A_c \Delta z} = - \frac{dC_A}{dt}$$

$$z \rightarrow 0 \quad \frac{dW_A}{dz} = - \frac{dC_A}{dt}$$

For dilute solution and constant total concentration :

$$W_A = -D_{AB} \frac{dC_A}{dz}$$

Gives :

$$D_{AB} \frac{d^2 C_A}{dz^2} = \frac{dC_A}{dt}$$

Let

$$\psi = \frac{C_A}{C_{A0}} \quad \text{gives} \quad D_{AB} \frac{d^2 \psi}{dz^2} = \frac{d\psi}{dt}$$

Boundary conditions :

$$t = t \text{ (present day)} \quad z = 0 \text{ (surface)}, \psi = 0$$

$$z = \infty, \quad \psi = 1$$

$$t = 0 \text{ (end of glacial)}, z > 0, \quad \psi = 1$$

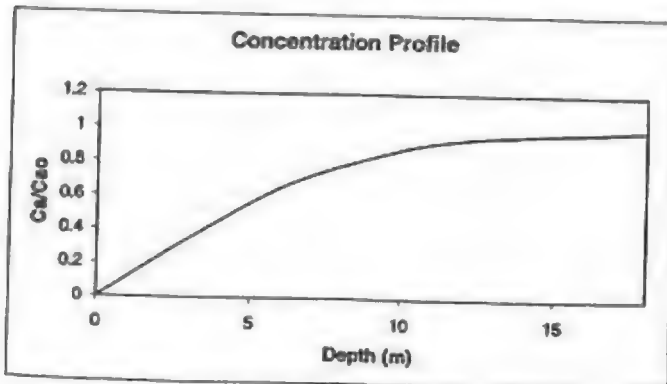
Gives the error function :

$$\psi = \text{erf} \frac{z}{\sqrt{4 D_{AB} t}} \quad \text{let} \quad \eta = \frac{z}{\sqrt{4 D_{AB} t}}$$

It is defined that at $\eta = 1.82$, $C_A = 0.01 C_{A0}$ and for $\eta > 1.82$, C_A is negligibly small.

This defines the penetration thickness, δ (as a function of time) :

$$1.82 = \frac{\delta}{\sqrt{4 D_{AB} t}}$$



P11-15cont'd

But the graph gives at , $C_A = 0.01 C_{A0} \rightarrow z = 0.4$ hence $\delta = 18 - 0.4 \text{ m}$, the penetration thickness after time t .

The time taken for δ to reach this thickness, is the time since the diffusion started (i.e. at the end of the last glacial)

$$t = \left(\frac{17.6}{1.82} \right)^2 \frac{1}{2 \times 2.64 \times 10^{-10}} \cdot \frac{1}{3600 \times 24 \times 365} = 5616 \text{ years}$$

P12-1 No solution will be given

P12-2

a) The rate of reaction ($\text{mol}/\text{dm}^3 \cdot \text{s}$) would decrease since $-r_a = \rho_c S_a (-r'_a)$. Using equation (12-32) we see that decreasing the surface area would decrease the Thiele modulus and thus increase η .

b) It really depends on the reaction order. If n is much larger than n' , then the catalyst weight will be underdesigned since $-r'_a < -r_a$ and $dW/dx = F_{A0}/-r_a$ in a PFR the weight will be smaller. Another problem is the dependence on temperature and activation energies which could become very destructive.

c) If the gas velocity were to increase the catalyst weight required would increase

$$W = \frac{v_0}{\Omega k S_a} \ln \frac{1}{1-X}$$

the length would then increase by the same factor:

$$L = \frac{W}{A_c \rho_b}$$

Increasing temperature would change the specific reaction rates which would cause the weight to decrease and the length to decrease.

d) In example 12-4, the reactor is 5m in diameter and 22m high whereas the reactor in example 12-6 is only 2 m³ in volume. The charge is much different. In 12-4 the charge is 100 kg/m³ whereas 12-6 it is only 3.9 kg.m³.

e) No solution will be given.

f)

$$\begin{aligned} C_{wp} &= \frac{-r_a \rho_c R^2}{D_c C_{As}} = \frac{k S_a \rho_c C_{NO} R^2}{D_c C_{As}} \\ &= \frac{(4.42 \times 10^{-10})(530)(3 \times 10^{-3})(0.0004)}{(1.89 \times 10^{-8})(0.02)} = 20 \end{aligned}$$

PI2-2 cont'd

$C_{ap} > 1$ so it is internal diffusion limited

$$\frac{k \rho_b S_g R n}{k_c C_{Ab}} = \frac{(4.42 * 10^{-10})(1.6 * 10^6)(530)(3 * 10^{-3})(.0004)}{(6 * 10^{-5})(0.02)}$$
$$= .33$$

$0.33 > 0.15$ so it is also external diffusion limited.

$$\left| \frac{-\Delta H(k S_A C_{No}) \rho_b R E}{h T^2 R_g} \right| =$$
$$\frac{(104.67)(4.42 * 10^{-10})(530)(0.004)(1.4 * 10^6)(3 * 10^{-3})(83.76)}{(105.5)(1651.73)^2 (.008314)}$$
$$= 4.37 * 10^{-5}$$

$4.37 * 10^{-5} < 0.15$ so the bulk temperature is the same as the temperature of the surface of the pellet.

g) With the increase in temperature, the rate of reaction will increase, this will cause the slope of C_p/R_p vs $1/m$, and therefore the resistance, to decrease.

h) No solution will be given

i) No solution will be given

j) No solution will be given.

k) If the diameter of the catalyst pellet were decreased, the value of the Thiele modulus would decrease, but β would not.

PI2-3

(a) Yes.

(b) All T, $F_{T0} = 10$ g moles/hr. the rate of reaction changes with flow rate and increases linearly with temperature.

(c) Yes.

(d) $T < 367$ K: $F_{T0} = 1000$ g mole/hr, 5000 gmole/hr

$T < 362$ K: $F_{T0} = 100$ g mole/hr.

(e) Yes.

P12-3 cont'd

(f) $T > 367 \text{ K}$: $F_{T0} = 1000 \text{ g mole/hr}$, 5000 g mol/hr

$T > 362 \text{ K}$: $F_{T0} = 100 \text{ g mole/hr}$.

$$(g) \Omega = \frac{\text{actual rate of reaction}}{\text{ideal rate of reaction}} = \frac{-r_A (\text{at } 362 \text{ K}, F_{T0} = 10 \text{ g mol/hr})}{-r_A (\text{at } 362 \text{ K}, F_{T0} = 5000 \text{ g mol/hr})}$$

$$\Omega = \frac{0.26}{0.70} = 0.37$$

(h) At $F_{T0} = 5000 \text{ g mole/hr}$, there is no external diffusion limitation, so the external effectiveness factor is one.

$$\eta = \frac{\text{actual rate of reaction (at } 362 \text{ K}, F_{T0} = 5000 \text{ g mol/hr})}{\text{extrapolated rate of reaction (at } 362 \text{ K}, F_{T0} = 5000 \text{ g mol/hr)}}$$

$$\eta = \frac{1.2}{1.4} = 0.86$$

$$(i) \eta = \frac{3[\phi \cosh \phi - 1]}{\phi^2} = 0.86$$

By iterative solution, $\phi = 1.60$

$$\phi = \frac{C_A}{C_{AS}} = \left(\frac{1}{\lambda}\right) \frac{\sinh(\phi \lambda)}{\sinh \phi}$$

P12-4 No solution will be given

P12-5

Curve A is reaction-rate limited. This is so because of the way the curve bends implying an exponential function which is also the equation for k of a reaction with respect to temperature.

Curve B is inter-diffusion limited. This is because it has a dependence on temperature, but not a real significant

Curve C is outer-diffusion limited. This has a much larger dependence on temperature.

P12-6

$$\text{If } \varphi = \frac{C_A}{C_{AS}}, \lambda = \frac{r}{R}, \phi_n^2 = \frac{kn R^2 S_a \rho_b C_{AS}^{n-1}}{D_c}$$

$$\text{Then } \varphi = \left(\frac{1}{\lambda} \right) \frac{\sinh \phi_1 \lambda}{\sinh \phi_1}$$

$$\begin{array}{ll} \text{Boundary} & \varphi = (\lambda = 1) = 1 \\ \text{conditions:} & \varphi = (\lambda = 0) = \text{finite} \end{array}$$

$$\text{Effectiveness factor: } \eta = \frac{3}{\phi_1^2} (\phi_1 \cosh \phi_1 - 1) \text{ first order reaction.}$$

$$\text{At } r = \frac{R}{2}, \lambda = \frac{1}{2}, C_A = 0.1 C_{AS} \text{ where } C_{AS} = 1 \times 10^{-3} \frac{\text{mole}}{\text{l}}$$

$$R = 1 \times 10^{-3} \text{ cm}$$

$$D_C = 0.1 \text{ cm}^2/\text{sec}$$

$$(a) \lambda = \frac{7 \times 10^{-4}}{1 \times 10^{-3}} = 0.7$$

$$\varphi = \left(\frac{1}{\lambda} \right) \left(\frac{\sinh \phi_1 \lambda}{\sinh \phi_1} \right)$$

$$\text{At } \lambda = \frac{1}{2}, \varphi = 0.1 : 0.1 = 2 \left[\frac{\sinh (\phi_1 / 2)}{\sinh (\phi_1)} \right] \Rightarrow \phi_1 = 6.0$$

$$\therefore \varphi = \frac{1}{0.7} \left[\frac{\sinh (6 \times 0.7)}{\sinh 6} \right]$$

$$\frac{C_A}{1 \times 10^{-3}} = \frac{1}{0.7} \left[\frac{e^{4.2} - e^{-4.2}}{e^6 - e^{-6}} \right]$$

$$C_A = 2.36 \times 10^{-4} \frac{\text{g mol}}{\text{l}}$$

P12-6 cont'd

$$(b) \quad \eta = \frac{3}{\phi_1^2} [\phi_1 \cosh \phi_1 - 1] = 0.80 \Rightarrow \phi_1 = 2.04$$

$$\phi_1^2 = \frac{k R^2 S_A \rho_B}{D_e}$$

$$\text{At } \lambda = \frac{1}{2}, \quad \phi = 0.1 : \phi_1 = 6 \text{ (see part (a))}$$

12-7

a) Start with a mole balance:

$$WA|_z - WA|_{z+\Delta z} + r_A A \Delta z = 0$$

Divide by $A \Delta z$ and take the limit as $\Delta z \rightarrow 0$.

$$\frac{dW}{dz} - r_A = 0$$

From the flux equation:

$$W = -D_e \frac{dC_A}{dz}$$

Combining the two equations we get:

$$\frac{d[-D_e dC_A/dz]}{dz} + k = 0$$

Dividing by $-D_e$ we get:

$$\frac{d^2 C_A}{dz^2} + \frac{k}{D_e} = 0$$

We need boundary conditions

$$\text{B.C. (1):} \quad \frac{dC_A}{dz} = 0 @ z = L$$

$$\text{B.C. (2):} \quad C_A = C_{A0} @ z = 0$$

P12-7 cont'd

We can then solve for the concentration profile:

$$\frac{dC_A}{dz} = \frac{kz}{D_e} + C_1$$

Using boundary condition (1):

$$0 = \frac{kL}{D_e} + C_1$$

$$C_1 = -\frac{kL}{D_e}$$

$$\frac{dC_A}{dz} = \frac{kz}{D_e} - \frac{kL}{D_e}$$

Integrating again:

$$dC_A = \left(\frac{kz}{D_e} - \frac{kL}{D_e} \right) dz$$

$$C_A = \frac{k}{2D_e} z^2 - \frac{kL}{D_e} z + C_2$$

From boundary condition 2 $C_{A0} = C_2$

$$C_A = \frac{k}{2D_e} z^2 - \frac{kL}{D_e} z + C_{A0}$$

(b) $\eta = \frac{\text{rate of reaction with diffusion}}{\text{rate of reaction without diffusion}}$

$$\eta = \frac{\frac{2D(C_A - C_{A0})}{z(z-2L)}}{k} = \frac{2D(C_A - C_{A0})}{kz(z-2L)}$$

(c) Boundary conditions: $C_A = 0$ at $z = L$

$$0 = \frac{kL}{D} \left(\frac{L}{2} - L \right) + C_{A0}$$

$$C_{A0} = \frac{kL^2}{2D}$$

P12-7 cont'd

$$L = \sqrt{\frac{2D C_{A0}}{k}} = \sqrt{\frac{2(3.6 \times 10^{-6} \text{ cm}^2/\text{s})(4.36 \times 10^{-5} \text{ mol/cm}^3)}{(2.3 \times 10^{-15} \text{ mol/s})/(3 \times 10^{-10} \text{ cm}^2)(\text{L cm})}}$$

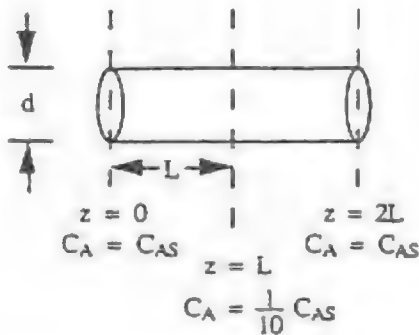
$$L^{1/2} = 0.0640$$

$$L = 0.0041 \text{ cm} = 41 \mu\text{m}$$

(d) The answer in part (c) is equal to the average tail length..

$\eta = 1$ in this problem. If $\eta = 1$, then it contradicts the assumption of diffusion being rate-limiting.

P12-8



First-order irreversible reaction: $A \rightarrow B$

$$-r_A = k C_A$$

$$W_A = -D \frac{dC_A}{dz}$$

$$\text{Mole balance: } -\frac{\pi d^2}{4} \frac{d}{dz} \left(\frac{dW_A}{dz} \right) + \pi d r_A = 0$$

$$\frac{d}{dz} D \left(\frac{d^2 C_A}{dz^2} \right) - k C_A = 0$$

$$\frac{C_{AS}}{L^2} \left(\frac{d^2 \psi}{d\lambda^2} \right) - \left(\frac{4k}{Dd} \right) C_{AS} \psi = 0$$

$$\Rightarrow \Phi^2 = \left(\frac{4k L^2}{Dd} \right)$$

P12-8 cont'd

Concentration distribution: $C_A = C_{AS} \left(\frac{\cosh \left[\phi \left(1 - \frac{z}{L} \right) \right]}{\cosh \phi} \right)$

$L = 10^{-3} \text{ cm}, 2L = 2 \times 10^{-3} \text{ cm}$

$C_{AS} = 10^{-3} \text{ g mole/l}$

$D = 0.1 \text{ cm}^2/\text{sec}$

At $z = L, C_A = \frac{1}{10} C_{AS} = C_{AS} \left(\frac{\cosh \left[\phi \left(1 - \frac{L}{L} \right) \right]}{\cosh \phi} \right)$

$\frac{1}{10} = \frac{1}{\cosh \phi}$

$\phi = 2.9932$

(a) At $z = 1/2 L: C_A = C_{AS} \left(\frac{\cosh \left[\phi \left(1 - \frac{0.5L}{L} \right) \right]}{\cosh \phi} \right)$

$C_A = (0.001) \left(\frac{\cosh [2.9932(0.5)]}{\cosh (2.9932)} \right)$

$C_A = 2.345 \times 10^{-4} \text{ g mol/l}$

(b) $\phi = 2L \sqrt{\frac{k}{Dd}} \Rightarrow \phi \propto (2L)$

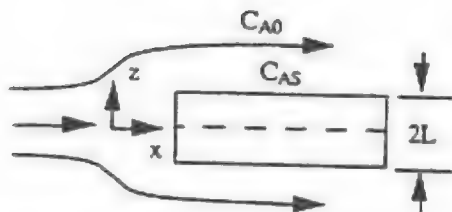
$\eta_{\text{old}} = \frac{\tanh \phi_{\text{old}}}{\phi_{\text{old}}} = \frac{\tanh (2.9932)}{2.9932} = 0.3324$

$\eta_{\text{new}} = 0.8 = \frac{\tanh \phi_{\text{new}}}{\phi_{\text{new}}} \Rightarrow \phi_{\text{new}} = 0.8880$

$2L_{\text{new}} = 2L_{\text{old}} \left(\frac{\phi_{\text{new}}}{\phi_{\text{old}}} \right) = (2 \times 10^{-3}) \left(\frac{0.8880}{2.9932} \right) = 5.993 \times 10^{-4} \text{ cm}$

(c) At $z = L, C_A = \frac{C_{AS}}{\cosh \phi_{\text{new}}} = \frac{0.001}{\cosh (0.8880)} = 7.038 \times 10^{-4} \text{ g mol/l}$

Thus minimum C_A is now 70.38% of C_{AS} . Therefore the suggestion is plating entire surface of the inside of the pore.



Define $W_A > 0$ in direction of increasing z

Material balance:

$$W_A A_P l_z - W_A A_P l_{z+\Delta z} + (-r_A^-) a A_P \Delta z = 0$$

$$-r_A^- = k C_A; W_A = -D_e \frac{dC_A}{dz} + C_A V \approx -D_e \frac{dC_A}{dz} \text{ for small } C_A$$

$$\text{Taking } \Delta z \rightarrow 0: -A_P \frac{dW_A}{dz} + r_A^- a A_P = 0$$

$$A_P \frac{d}{dz} \left(D_e \frac{dC_A}{dz} \right) - k C_A a A_P = 0$$

$$\text{For constant } D_e; D_e \frac{d^2 C_A}{dz^2} - k C_A a = 0$$

$$\text{Boundary conditions: } z = L \quad C_A = C_{AS}$$

$$z = 0 \quad \frac{dC_A}{dz} = 0 \text{ by symmetry}$$

$$\frac{d^2 C_A}{dz^2} - \alpha^2 C_A = 0 \quad \text{where } \alpha^2 = \frac{k a}{D_e}$$

$$\text{Assume } C_A = e^{rz}, \text{ then } r^2 - \alpha^2 = 0 \quad r = \pm \alpha$$

$$C_A = A_1 e^{-\alpha z} + A_2 e^{\alpha z}$$

$$\text{At } z = L: C_{AS} = A_1 e^{-\alpha L} + A_2 e^{\alpha L}$$

$$\left. \frac{dC_A}{dz} \right|_{z=0} = 0 = -\alpha A_1 + \alpha A_2 = 0$$

$$\therefore A_1 = A_2$$

$$\text{From above: } A_1 = \frac{C_{AS}}{e^{-\alpha L} + e^{\alpha L}}$$

$$C_A = C_{AS} \left(\frac{e^{-\alpha L} + e^{\alpha L}}{e^{-\alpha L} + e^{\alpha L}} \right)$$

Therefore, concentration profile can be written as:

$$C_A = C_{AS} \left\{ \frac{\cosh(\alpha z)}{\cosh(\alpha L)} \right\}$$

$$W_A A_p = -D_e \left(\frac{dC_A}{dz} \right)_{z=L} A_p = -A_p D_e C_{AS} \alpha \left(\frac{\sinh(\alpha z)}{\cosh(\alpha L)} \right)_{z=L}$$

$$W_A A_p = -A_p D_e \alpha C_{AS} \tanh(\alpha L)$$

By the sign convention: $-W_A A_p = \eta r_A' a A_p L = -\eta k C_{AS} a A_p L$

$$\therefore \eta k C_{AS} a A_p L = A_p D_e \alpha C_{AS} \tanh(\alpha L)$$

$$\eta = \left(\frac{\alpha D_e}{k a L} \right) \tanh(\alpha L) = \sqrt{\frac{k a}{D_e}} \left(\frac{D_e}{k a} \right) \frac{1}{L} \tanh \left(\sqrt{\frac{k a}{D_e}} L \right)$$

$$\eta = \left(\sqrt{\frac{D_e}{k a}} \frac{1}{L} \right) \tanh(\alpha L) \left(\sqrt{\frac{k a}{D_e}} L \right)$$

Overall effectiveness factor: $-W_A A_p = \Omega k C_{A0} a A_p L = \eta k C_{AS} a A_p L$

or: $\frac{\Omega}{\eta} = \frac{C_{AS}}{C_{A0}}$

$$-W_A A_p = k_C A_p (C_{A0} - C_{AS}) = \alpha A_p D_e C_{AS} \tanh(\alpha L)$$

$$C_{A0} = C_{AS} \left[1 + \frac{\alpha D_e}{k_C} \tanh(\alpha L) \right]$$

$$\frac{C_{AS}}{C_{A0}} = \left[\frac{1}{1 + \frac{\alpha D_e}{k_C} \tanh(\alpha L)} \right]$$

$$\Omega = \frac{\eta}{1 + \frac{\alpha D_e}{k_C} \tanh(\alpha L)} = \frac{\left(\sqrt{\frac{D_e}{k a}} \frac{1}{L} \right) \tanh \left(\sqrt{\frac{k a}{D_e}} L \right)}{1 + \sqrt{\frac{k a D_e}{k_C}} \tanh \left(\sqrt{\frac{k a}{D_e}} L \right)}$$

Start with the mole balance:

$$W_{A,z}A|_z - W_{A,z}A|_{z+\Delta z} + r_A A \Delta z = 0$$

Divide by $(-A\Delta z)$ and take the limit as Δz approaches zero.

$$\frac{dW_{A,z}}{dz} - r_A = 0$$

Then find the equation for the flux:

$$W_{A,z} = -D_e \frac{dC_A}{dz}$$

Combine and get the correct differential equation:

$$\frac{d}{dz} \left(-D_e \frac{dC_A}{dz} \right) + k = 0$$

$$\frac{d^2 C_A}{dz^2} - \frac{k}{D_e} = 0$$

The boundary conditions are as follows:

$$\text{B.C. 1: } dC_A/dz = 0 \text{ @ } z = 0$$

$$\text{B.C. 2: } C_A = C_{A_s} \text{ @ } z = L$$

We are then able to solve the equation:

$$\frac{dC_A}{dz} = \frac{kz}{D_e} + C_1$$

$$0 = C_1$$

$$C_A = \frac{kz^2}{2D_e} + C_2$$

$$C_{A_s} = \frac{kL^2}{2D_e} + C_2$$

P12-10cont'd

$$C_A = C_{A_s} + \frac{kz^2}{2D_e} - \frac{kL^2}{2D_e}$$

$$\frac{C_A}{C_{A_s}} = 1 + \frac{\Phi_0^2}{2} \left(\frac{z^2}{L^2} \right) - \frac{\Phi_0^2}{2} = 1 + \frac{\Phi_0^2}{2} \left(\frac{z^2}{L^2} - 1 \right)$$

b) $\Phi_0 = 1.414$ $\Phi_0^2 = 2$

$$0 = 1 + 1 \left(\frac{z^2}{L^2} - 1 \right)$$

$$z = 0$$

$\Phi_0 = 4$ $\Phi_0^2 = 16$

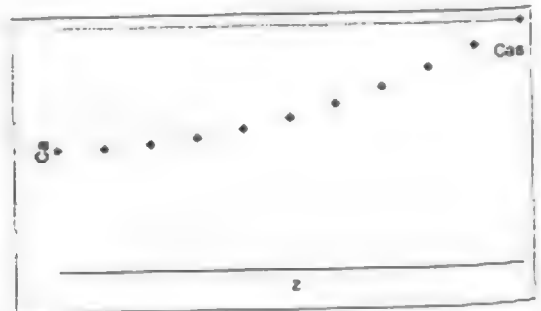
$$0 = 1 + 8 \frac{z^2}{L^2} - 8$$

$$7 = 8 \frac{z^2}{L^2}$$

$$z = 0.935 L$$

c)

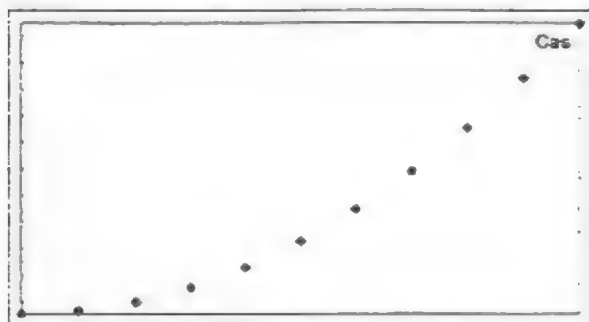
$$\frac{C_A}{C_{A_s}} = 1 + \frac{\Phi_0^2}{2} \left[\left(\frac{z}{L} \right)^2 - 1 \right]$$



for $\Phi_0^2 < 2$

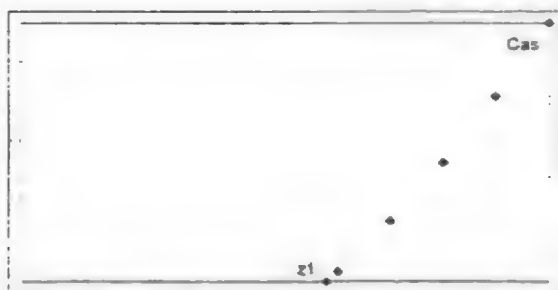
P12-10cont'd

for $\Phi_0^2 = 2$



for $\Phi_0^2 > 2$

where $z_1 = L \sqrt{1 - \frac{2}{\Phi_0^2}}$



$$\eta = \frac{\int_{z_1}^L -r_A A_C dz}{-r_{AS} A_C L}$$

when $\Phi_0^2 \leq 2$ then $z_1 = 0$. Then $\eta = 1$.

When $\Phi_0^2 > 2$ then $z_1 = L \sqrt{1 - \frac{2}{\Phi_0^2}}$

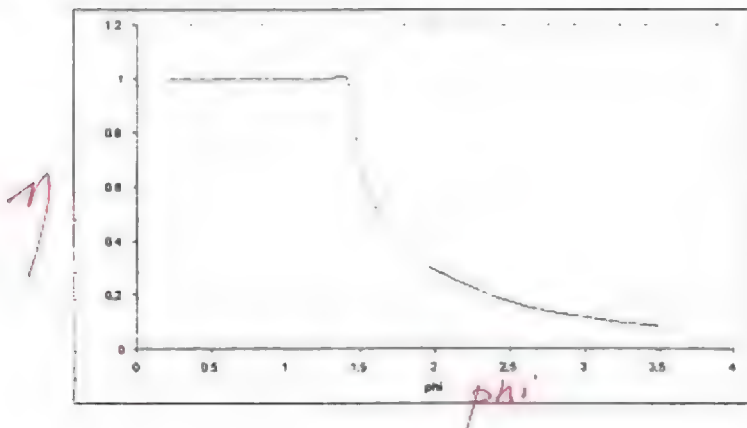
Then the integration goes like this:

P12-10cont'd

$$\eta = \frac{-r_A A_C L + r_A A_C L \left(1 - \frac{2}{\Phi_0^2}\right)^{\frac{1}{2}}}{-r_A A_C L}$$

$$= 1 - \left(1 - \frac{2}{\Phi_0^2}\right)^{\frac{1}{2}}$$

d)



e) Start with the mole balance:

$$W_{Ar} 4\pi r^2 \Big|_r - W_{Ar} 4\pi r^2 \Big|_{r+\Delta r} - r_A 4\pi r^2 \Delta r = 0$$

Then divide by $-4\pi\Delta r$ and take the limit as Δr approaches zero.

$$\frac{dW_{Ar} r^2}{dr} - r_A r^2 = 0$$

$$W_{Ar} = -D_e \frac{dC_A}{dr}$$

P12-10cont'd

Then find the equation for the flux:

$$\frac{d}{dr} \left(r^2 \frac{dC_A}{dr} \right) = \frac{k}{D_e} r^2$$

$$\int_0^r d \left(r^2 \frac{dC_A}{dr} \right) = \int_0^r \frac{k}{D_e} r^2 dr$$

$$r^2 \frac{dC_A}{dr} \Big|_{r=R} - r^2 \frac{dC_A}{dr} \Big|_{r=0} = \frac{k}{D_e} \frac{r^3}{3}$$

$$\frac{dC_A}{dr} = \frac{kr}{3D_e}$$

$$\int_{C_{AS}}^{C_A} dC_A = \frac{k}{3D_e} \int_R^r r dr$$

$$C_A - C_{AS} = \frac{kR^2}{6D_e} \left(1 - \left(\frac{r}{R} \right)^2 \right)$$

$$\frac{C_A}{C_{AS}} = 1 + \frac{\Phi_0^2}{6} \left[\left(\frac{r}{R} \right)^2 - 1 \right]$$

$$\text{where } \Phi_0^2 = \frac{kR^2}{D_e C_{AS}}$$

$$\Phi_0 = 1.414$$

$$\Phi_0^2 = 2$$

$$0 = 1 + \frac{2}{6} \left[\left(\frac{r}{R} \right)^2 - 1 \right]$$

$$\left(\frac{r}{R} \right)^2 = -2$$

This is not possible so C_A is going to finite non-zero everywhere.

$$\Phi_0 = 4$$

$$\Phi_0^2 = 16$$

$$0 = 1 + \frac{16}{6} \left[\left(\frac{r}{R} \right)^2 - 1 \right]$$

$$\left(\frac{r}{R} \right)^2 = -\frac{6}{16} + 1 = \frac{5}{8}$$

P12-10cont'd

Hence $C_A = 0$ at $r = R\sqrt{\frac{5}{8}}$

For $\Phi_0^2 \leq 6$

$$\eta = \frac{\int_0^R -r_A A_C dz}{-r_{AS} A_C R} \quad \text{where } z_1 = 0$$

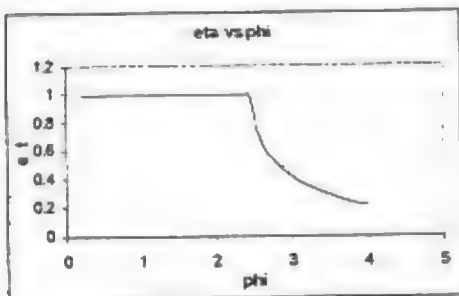
$$\eta = 1$$

For $\Phi_0^2 > 6$

$$\eta = \frac{\int_0^R -r_A A_C dz}{-r_{AS} A_C R}$$

$$= \frac{-r_A A_C R + r_A A_C R \left(1 - \frac{6}{\Phi_0^2}\right)^{\frac{1}{2}}}{-r_{AS} A_C R}$$

$$= 1 - \left(1 - \frac{6}{\Phi_0^2}\right)^{\frac{1}{2}}$$



P12-10cont'd

1) For cylinder

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{dC_A}{dr} \right) = \frac{k}{D_e}$$

$$\int_0^r \frac{d}{dr} \left(r \frac{dC_A}{dr} \right) = \frac{k}{D_e} \int_0^r r dr$$

$$r \frac{dC_A}{dr} \Big|_{r=r} - r \frac{dC_A}{dr} \Big|_{r=0} = \frac{k r^2}{2 D_e}$$

$$\frac{dC_A}{dr} = \frac{k r}{2 D_e}$$

$$\int_{C_{AS}}^{C_A} dC_A = \frac{k}{2 D_e} \int_0^r r dr$$

$$C_A - C_{AS} = \frac{k R^2}{4 D_e} \left[\left(\frac{r}{R} \right)^2 - 1 \right]$$

$$\frac{C_A}{C_{AS}} = 1 + \frac{k R^2}{4 D_e C_{AS}} \left[\left(\frac{r}{R} \right)^2 - 1 \right]$$

$$\frac{C_A}{C_{AS}} = 1 + \frac{\Phi_0^2}{4} \left[\left(\frac{r}{R} \right)^2 - 1 \right]$$

$$\text{where } \Phi_0^2 = \frac{k R^2}{D_e C_{AS}}$$

$$\Phi = 1.414$$

$$\Phi_0^2 = 2$$

$$0 = 1 + \frac{2}{4} \left[\left(\frac{r}{R} \right)^2 - 1 \right]$$

$$\left(\frac{r}{R} \right)^2 = -1$$

This is not possible so C_A will never be zero.

P12-10cont'd

$$\Phi = 4$$

$$\Phi_0^2 = 16$$

$$0 = 1 + \frac{16}{4} \left[\left(\frac{r}{R} \right)^2 - 1 \right]$$

$$\left(\frac{r}{R} \right)^2 = \frac{3}{4}$$

$$r = R \sqrt{\frac{3}{4}}$$

$$\text{For } \Phi_0^2 \leq 4$$

$$\eta = \frac{\int_0^R -r_A A_C dz}{-r_{AS} A_C R}$$

$$\text{where } z_1 = 0$$

$$\eta = 1$$

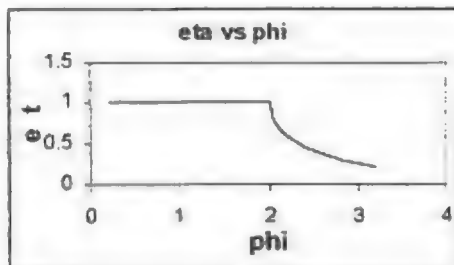
$$\text{For } \Phi_0^2 > 4$$

$$\eta = \frac{\int_{z_1}^R -r_A A_C dz}{-r_{AS} A_C R}$$

$$= \frac{-r_A A_C R + r_A A_C R \left(1 - \frac{4}{\Phi_0^2} \right)^{\frac{1}{2}}}{-r_{AS} A_C R}$$

$$\text{where } z_1 = \left(1 - \frac{4}{\Phi_0^2} \right)^{\frac{1}{2}}$$

$$= 1 - \left(1 - \frac{4}{\Phi_0^2} \right)^{\frac{1}{2}}$$



12-18

P12-11 Given: second-order decomposition reaction: $A \rightarrow B + 2C$

$$k = 50 \text{ m}^6/\text{g sec mol}; d_p = 0.4 \text{ cm}; U = 3 \text{ m/s}; T = 250^\circ\text{C} = 523^\circ\text{K};$$

$$P = 500 \text{ kPa} = 4.936 \text{ atm}; X = 0.80; D_e = 2.66 \times 10^{-8} \text{ m}^2/\text{s}; E_b = 0.4;$$

$$\rho_b = 2 \times 10^6 \text{ g/m}^3; S_a = 400 \text{ m}^2/\text{g}.$$

$$C_{A0} = \frac{P}{RT} = \frac{4.936 \text{ atm}}{\left(0.082 \frac{\text{L atm}}{\text{g mol } ^\circ\text{K}}\right) 523^\circ\text{K}} = 0.115 \frac{\text{g mol}}{\text{L}}$$

$$\text{Rate law: } -r_A = k C_A^2$$

Mole balance: equation (11-65) from the text.

$$D_{AB} \frac{d^2 C_A}{dz^2} - U \frac{dC_A}{dz} + r_A \rho_B = 0$$

$$D_{AB} \frac{d^2 C_A}{dz^2} - U \frac{dC_A}{dz} - \Omega k S_A \rho_B C_A^2 = 0$$

Neglecting axial diffusion with respect to forced axial convection, we have:

$$\frac{dC_A}{dz} = - \left(\frac{\Omega k S_A \rho_B}{U} \right) C_A^2$$

$$- \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^2} = \left(\frac{\Omega k S_A \rho_B}{U} \right) \int_0^z dz$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = \left(\frac{\Omega k S_A \rho_B}{U} \right) z$$

$$\text{At } z = L: \quad \frac{1}{C_{A0}} = \left(\frac{1}{1-X} - 1 \right) = \left(\frac{-2\rho_B k S_A}{U} \right) L$$

$$L = \left(\frac{U}{\Omega \rho_B k S_A C_{A0}} \right) \left(\frac{1}{1-X} - 1 \right)$$

Internal effective factor:

$$\eta = \left(\frac{2}{n+1} \right)^{1/2} \frac{3}{\phi_n} \text{ where } n = 2$$

$$\phi_2 = R \sqrt{\frac{k S_A \rho_B C_{A0}}{D_e}}$$

P12-11cont'd

$$\phi_2 = 0.2 \times 10^{-2} \text{ m} \sqrt{\frac{\left(50 \frac{\text{m}^2}{\text{g s mol}}\right) \left(400 \frac{\text{m}^2}{\text{g}}\right) \left(2 \times 10^6 \frac{\text{g}}{\text{m}^3}\right) \left(0.115 \frac{\text{g mol}}{\text{l}}\right) \left(\frac{10^3 \text{ l}}{\text{m}^3}\right)}{2.66 \times 10^{-8} \frac{\text{m}^2}{\text{s}}}}$$

$$\phi_2 = 2.63 \times 10^7 \text{ very large}$$

$$\eta = \left(\frac{2}{2+1}\right)^{1/2} \frac{3}{2.63 \times 10^7} = 9.313 \times 10^{-8}$$

$$\text{Internal-diffusion limited: } \Omega = \eta = 9.313 \times 10^{-8}$$

Reactor length:

$$L = \frac{3 \text{ m/s} \left(\frac{1}{1-0.8} - 1\right)}{\left(9.313 \times 10^{-8}\right) 2 \times 10^6 \frac{\text{g}}{\text{m}^3} \left(50 \frac{\text{m}^2}{\text{g s mol}}\right) \left(400 \frac{\text{m}^2}{\text{g}}\right) \left(115 \frac{\text{g mol}}{\text{m}^3}\right)}$$

$$L = 2.80 \times 10^{-5} \text{ m}$$

P12-12

a) Start with the mole balance taken on a shell

$$W_A 2\pi r \Big|_z - W_A 2\pi r \Big|_{z+\Delta z} + r'_A \rho_c 2\pi r \Delta z = 0$$

Divide by $-2\pi \Delta z$ and take the limit as Δz approaches zero to get:

$$\frac{d(W_A r)}{dr} - r'_A \rho_c r = 0$$

Next find the equation for equimolar counterdiffusion and plug it into the above equation:

$$\frac{d\left(r\left(-D_c \frac{dC_A}{dr}\right)\right)}{dr} - r'_A \rho_c r = 0$$

Next differentiate to get the following differential equation:

$$\frac{d^2 C_A}{dr^2} + \frac{1}{r} \frac{dC_A}{dr} - \frac{k_p \rho_c S_a C_A}{D_e} = 0$$

We can then set the following:

$$\varphi = \frac{C_A}{C_{A_s}}$$

$$\lambda = \frac{r}{R}$$

$$\frac{d^2 \varphi}{d\lambda^2} + \frac{1}{\lambda} \frac{d\varphi}{d\lambda} - \frac{k_p \rho_c S_a R^2}{D_e} \varphi = 0$$

$$\Phi_0^2 = \frac{k_p \rho_c S_a R^2}{D_e}$$

$$\lambda^2 \frac{d^2 \varphi}{d\lambda^2} + \lambda \frac{d\varphi}{d\lambda} - \Phi_0^2 \lambda^2 \varphi = 0$$

Solution:

$$\varphi = C_1 I_0(\Phi \lambda) + C_2 K_0(\Phi \lambda)$$

Boundary Conditions:

$$\varphi = 1 @ \lambda = 1$$

$$\frac{d\varphi}{d\lambda} = 0 @ \lambda = 0$$

$$\frac{d\varphi}{d\lambda} = \Phi [C_1 I_1(\Phi \lambda) - C_2 K_1(\Phi \lambda)]$$

$$I_1(0) = 0$$

$$K_1(0) = \infty$$

$$\text{as } \frac{d\varphi}{d\lambda} \Big|_{\lambda=0} \rightarrow 0 \Rightarrow C_2 = 0$$

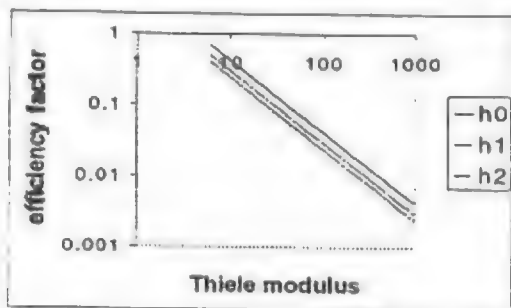
$$\varphi = C_1 I_0(\Phi \lambda)$$

$$1 = C_1 I_0(\Phi) \Rightarrow C_1 = \frac{1}{I_0(\Phi)}$$

$$\varphi = \frac{I_0(\Phi \lambda)}{I_0(\Phi)}$$

P12-13

As can be seen by this graph, all of the lines do not coalesce into one line, but are in fact three different lines

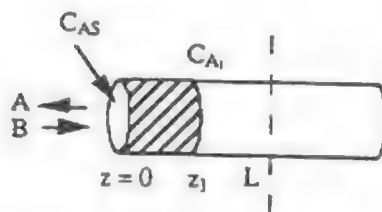


P12-14 No solution will be given

P12-15 No solution will be given

P12-16 No solution will be given

P12-17



Given: $A \leftrightarrow B$ on the walls of a cylindrical catalyst pore.

z_1 = length of poisoned section

$$-r_A' = k C_A$$

P12-17 cont'd

(a) In the poisoned section:

$$W_A \pi r^2|_z - W_A \pi r^2|_{z+\Delta z} + r_A'' P \Delta z = 0$$

For $0 \leq z \leq z_1$, $r_A'' = 0$, since this area is poisoned.

$$W_A \pi r^2|_z - W_A \pi r^2|_{z+\Delta z} = 0 \quad \text{or} \quad \frac{dW_A}{dz} = 0$$

$$W_A = -CD_{AB} \frac{dX_A}{dz} + X_A (W_A + W_B)$$

But $W_A = -W_B$, since, for each mole of A consumed, one mole of A is reacted.

$$W_A = -CD_{AB} \frac{dX_A}{dz} \quad \text{and} \quad \frac{d}{dz} \left(CD_{AB} \frac{dX_A}{dz} \right) = 0 \quad \text{or} \quad \frac{d^2 X_A}{dz^2} = 0$$

$$\text{At } z=0, \quad C_A = X_{AS} C = C_{AS}$$

$$\text{At } z = z_1, \quad C_A = X_{A1} C = C_{A1}$$

$$\text{Integrating:} \quad X_{A1} = K_1 z + K_2$$

$$\text{At } z=0, \quad X_A = \frac{C_{AS}}{C}; \quad K_2 = \frac{C_{AS}}{C}$$

$$\text{at } z = z_1, \quad X_A = X_{A1} = \frac{C_{A1}}{C} = k_1 z_1 + \frac{C_{AS}}{C} \Rightarrow k_1 = \frac{C_{A1} - C_{AS}}{C z_1}$$

$$X_A = \frac{C_A}{C} = \frac{C_{A1} - C_{AS}}{C z_1} z + \frac{C_{AS}}{C}$$

$$C_A = (C_{A1} - C_{AS}) \left(\frac{z}{z_1} \right) + C_{AS}$$

$$\text{The flux is } W_A = -CD_{AB} \frac{dX_A}{dz} = -D_{AB} \frac{dC_A}{dz} (C_{A1} - C_{AS})$$

$$(b) \text{ Before poisoning, } \eta = \frac{\tanh \phi_1}{\phi_1} \quad \text{where } \eta = \phi_1 = L \left(\frac{2k''}{r D_{AB}} \right)^{1/2}$$

After poisoning, the differential equation and boundary conditions are the same for the unpoisoning region of the pore. $z_1 \leq z \leq L$ if z is replaced by $L - z$ and if we let

$C_A = C_{A1}$ at $z' = 0$ and $\frac{dC_A}{dz} = 0$ at $z = L - z_1$. then, for the unpoisoned section of the

catalyst pore η applies if ϕ is replaced by :

$$(L - z_1) \left(\frac{2k''}{r D_{AB}} \right)^{1/2} = \left(1 - \frac{z_1}{L} \right) \phi_1, \text{ i.e., } \eta = \frac{\tanh \left[\phi_1 \left(1 - \frac{z_1}{L} \right) \right]}{\phi_1 \left(1 - \frac{z_1}{L} \right)}$$

P12-17 cont'd

The effectiveness factor for the unpoisoned section of catalyst pore is defined as :

$$W_A = \eta \pi r (L - z) C_{A1}$$

This can be related to the overall effectiveness factor for the entire pore by

$$W_A = \eta' \pi r L C_{AS} = \eta \pi r L C_{A1}$$

$$\therefore \eta' C_{AS} = \eta C_{A1} \left(1 - \frac{z_1}{L}\right)$$

$$\text{But } W_A = -\frac{D_{AB}}{z_1} (C_{A1} - C_{AS}) \text{ from part (a)}$$

$$\therefore C_{A1} = C_{AS} - \frac{W_A z_1}{D_{AB}}$$

$$\therefore \eta' C_{AS} = \eta \left(1 - \frac{z_1}{L}\right) \left[C_{AS} - \frac{W_A z_1}{D_{AB}}\right]$$

$$\text{But } W_A \pi r^2 = \eta' 2\pi r L C_{AS} k''$$

$$\eta' = \eta \left(1 - \frac{z_1}{L}\right) \left(1 - \frac{2\eta' L^2 C_{AS} k'' z_1}{r D_{AB} L}\right)$$

$$\eta' = \eta \left(1 - \frac{z_1}{L}\right) \left(1 - \eta' \left(\frac{z_1}{L}\right) \phi^2\right)$$

$$\eta' = \frac{\eta \left(1 - \frac{z_1}{L}\right)}{1 + \phi_1^2 \eta \left(1 - \frac{z_1}{L}\right) \left(\frac{z_1}{L}\right)} = \frac{\left(1 - \frac{z_1}{L}\right) \left[\frac{\tanh\left\{\phi_1 \left(1 - \frac{z_1}{L}\right)\right\}}{\phi_1 \left(1 - \frac{z_1}{L}\right)} \right]}{1 + \phi_1^2 \eta \left(1 - \frac{z_1}{L}\right) \left(\frac{z_1}{L}\right) \left[\frac{\tanh\left\{\phi_1 \left(1 - \frac{z_1}{L}\right)\right\}}{\phi_1 \left(1 - \frac{z_1}{L}\right)} \right]}$$

$$\eta' = \frac{\tanh\left\{\phi_1 \left(1 - \frac{z_1}{L}\right)\right\}}{\phi_1 + \phi_1^2 \left(\frac{z_1}{L}\right) \tanh\left\{\phi_1 \left(1 - \frac{z_1}{L}\right)\right\}}$$

P12-18 The reaction is $A \rightarrow \frac{1}{2} A_2$

$$(a) \delta = \frac{1}{2} - 1 = -\frac{1}{2}; \quad \varepsilon = y_{A0} \delta = -0.5$$

$$C_A = \frac{C_{A0}(1 - X)}{(1 - 0.5X)} \quad \text{where } C_{A0} = \frac{P}{RT} = \frac{8.2 \text{ atm}}{\frac{0.0821 \text{ atm}}{\text{g mol}^\circ\text{K}} (227 + 273 \text{ K})} = 0.2 \frac{\text{g mol}}{\text{l}}$$

P12-18cont'd

$$y_A = \frac{F_A}{F_A + F_{A2}} = \frac{F_A}{F_A + \frac{1}{2}(F_{A0} - F_A)} = \frac{2F_A}{F_A + F_{A0}}$$

$$\frac{1}{y_A} = \frac{1}{2} + \frac{1}{2} \frac{F_{A0}}{F_A}$$

$$\frac{F_{A0}}{F_A} = 2\left(\frac{1}{y_A} - \frac{1}{2}\right) \quad \text{or} \quad \frac{F_A}{F_{A0}} = \frac{1}{\frac{2}{y_A} - 1} = \frac{y_A}{2 - y_A}$$

$$X = 1 - \frac{F_A}{F_{A0}} = 1 - \frac{y_A}{2 - y_A} = \frac{2 - 2y_A}{2 - y_A}$$

$$r_A = \frac{F_{A0} X}{W} \quad \text{where } W = 4 \times 40g = 160g = 0.16 \text{ kg}$$

$$r_A = k C_A^\alpha$$

$$\ln(-r_A) = \ln k_0 + \alpha \ln C_A$$

$$\text{Let } M = \ln(-r_A); \quad A_0 = \ln k_0; \quad A_1 = \alpha; \text{ and } N = \ln C_A$$

$$\therefore M = A_0 + A_1 N \quad (1)$$

$$\sum_i^n M_i = nA_0 + A_1 \sum_i^n N_i \quad (2)$$

$$\sum_i^n M_i N_i = A_0 \sum_i^n N_i + A_1 \sum_i^n N_i^2 \quad (3)$$

i	F _{Tn}	y _A	X	C _A	-r _A	M	N	N ²	MN
1	1	0.21	0.88	4.285 × 10 ⁻²	5.5	1.705	-3.150	9.923	-5.371
2	2	0.33	0.80	6.666 × 10 ⁻²	10	2.303	-2.708	7.333	-6.236
3	4	0.40	0.75	8 × 10 ⁻²	18.75	2.931	-2.526	6.381	-7.404
4	6	0.57	0.60	1.143 × 10 ⁻¹	22.5	3.114	-2.169	4.704	-6.754
5	11	0.70	0.46	1.403 × 10 ⁻¹	31.625	3.454	-1.964	3.857	-6.784
6	20	0.81	0.32	1.619 × 10 ⁻¹	40	3.689	-1.821	3.315	-6.717
					$\sum_i^n =$	17.196	-14.338	35.513	-39.266

Equations (2) and (3) become:

$$17.196 = 6A_0 - 14.338 A_1$$

$$-39.266 = -14.338 A_0 + 35.513 A_1$$

P12-18cont'd

$$\therefore A_0 = 6.36 = \ln k_0 \rightarrow k_0 = 578.25$$

$$A_1 = 1.46 \equiv 1.5 = \alpha$$

$$\text{At } T_1 = 237^\circ\text{C} = 510\text{ K}: k_1 = \frac{-r_A}{C_A^{1.5}}$$

$$-r_A = \frac{F_{A0} X}{W} \text{ where } X = \frac{2 - 2(0.097)}{2 - 0.097} = 0.9490$$

$$-r_A = \frac{(9)(0.9490)}{0.16} = 53.38 = k_1 C_A^{1.5} \text{ where:}$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{8.2}{0.082(510)} = 0.196 \frac{\text{g mol}}{\text{l}}$$

$$C_A = \frac{0.196(1 - 0.9490)}{1 - 0.5(0.9490)} = 0.019 \frac{\text{g mol}}{\text{l}}$$

$$k_1 = \frac{53.38}{(0.019)^{1.5}} = 2.035 \times 10^4$$

$$k_1 = k_0 \exp \left\{ \frac{E}{R} \left(\frac{1}{T_0} - \frac{1}{T_1} \right) \right\}$$

$$2.035 \times 10^4 = 578.25 \exp \left\{ \frac{E (\text{J/mole})}{8.314} \left(\frac{1}{500} - \frac{1}{510} \right) \right\}$$

$$\therefore E = 7.55 \times 10^5 \frac{\text{J}}{\text{g mol}}$$

$$(b) n_{\text{true}} = 2n_{\text{app}} - 1 = 2(1.5) - 1 = 2: \text{ second order}$$

$$E_{\text{true}} = 2E_{\text{app}} = 15.1 \times 10^5 \frac{\text{J}}{\text{mol}}$$

$$(c) \Phi_2 = R \sqrt{\frac{k S_a \rho_b C_{A0}}{D_e}} = \sqrt{\frac{(1 \times 10^{-2})^2 (2.035 \times 10^4) 49 (2.3 \times 10^6) 0.196}{0.23 \times 10^{-4}}}$$

$$\Phi_2 = 1.40 \times 10^6$$

$$\eta = \left(\frac{2}{n+1} \right)^{1/2} \left(\frac{3}{\Phi_n} \right) = \left(\frac{2}{2+1} \right)^{1/2} \left(\frac{3}{1.40 \times 10^6} \right) = 1.75 \times 10^{-6}$$

(d) To make the catalyst more effective, we should use smaller diameter.

12-26

P12-18cont'd

$$(c) C_A = 0.01 \frac{\text{g mole}}{\text{l}}; T = 527^\circ\text{C} = 800 \text{ K}$$

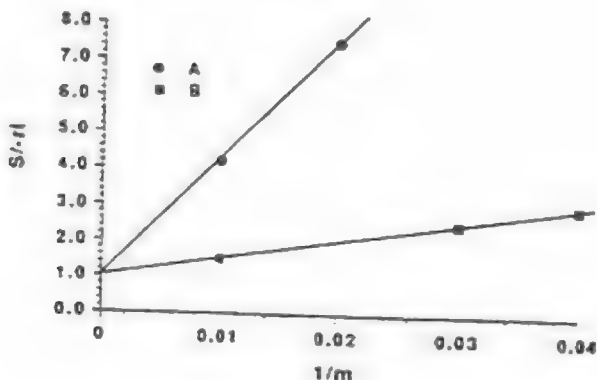
$$k = k_0 \exp \left(\frac{E}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right) = 578.25 \exp \left(\frac{7.55 \times 10^5}{8.314} \left(\frac{1}{500} - \frac{1}{800} \right) \right)$$

$$k = 2.19 \times 10^{32}$$

$$-r_A = k C_A^{1.5} = 2.19 \times 10^{32} (0.01)^{1.5} = 2.19 \times 10^{29} \frac{\text{g mole}}{\text{l s}}$$

P12-19

$$(a) \frac{-S}{r_L} = \frac{1}{k_b a_b} + \frac{1}{k\eta} \frac{1}{m}$$



$$\text{Slope A} = \frac{7.5 - 4.2}{0.01} = 330 = \frac{1}{k\eta_A}$$

$$\text{Slope B} = \frac{3 - 2.5}{0.01} = 50 = \frac{1}{k\eta_B}$$

Therefore, catalyst size A has smaller effectiveness factor than catalyst size B, since the k 's are equal.

P12-19 cont'd

- (b) From the figure above, r_{cr} depends on particle size, which means surface reaction rate does not control. Diffusion is the major resistance for particle size A.

$$\frac{1}{m} = \frac{1 \text{ dm}^3}{50 \text{ g}} = 0.02 \frac{\text{dm}^3}{\text{g}}$$

$$\text{intercept A} = r_b = 0.9 \text{ min.}$$

$$\% \text{ gas absorption} = \frac{0.9}{7.5} \times 100\% = 12\%$$

$$\% \text{ internal diffusion} = \frac{7.5 - 0.9}{7.5} \times 100\% = 88\%$$

Since internal diffusion is the controlling step, if a more efficient sparger were used, a significant increase in reaction would not be obtained.

$$(c) \quad \frac{\left(\frac{S}{-r_1}\right) - r_b}{\left(\frac{S}{-r_L}\right)} \times 100\% = 50\%$$

From the graph above, intercept $r_b = 1 \text{ min.}$

$$\frac{\left(\frac{S}{-r_2}\right) - 1}{\left(\frac{S}{-r_2}\right)} \leq 0.5 \quad \therefore \left(\frac{S}{-r_2}\right) \leq 2 \text{ min}$$

$$2 \text{ min} = 50 \frac{1}{m} + 1 \text{ min}$$

$$\frac{1}{m} = 0.02 \frac{\text{dm}^3}{\text{g}} \quad \text{or} \quad m = 50 \frac{\text{g}}{\text{dm}^3}$$

$$\text{The minimum catalyst charge is } 50 \frac{\text{g}}{\text{dm}^3}$$

P12-20

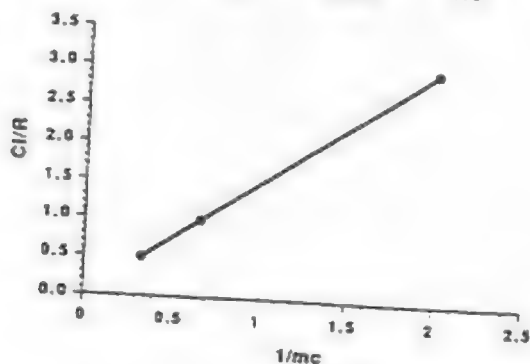
$$\frac{C_i}{R} = \frac{1}{k_b a_b} + \frac{1}{m_0} \left[\frac{1}{k_c a_c} + \frac{1}{\eta k} \right]$$

species i representing H₂

12-28

P12-20 cont'd

Run	P_i (atm)	C_i (gmol/dm ³)	R (gmol/ dm ³ min)	m_c (g/dm ³)	$1/m_c$ (dm ³ /g)	C_i/R (min.)	d_p (μ m)
1	3	0.007	0.014	3.0	0.333	0.5	12
2	18	0.042	0.014	0.5	2.000	3.0	50
3	3	0.007	0.007	1.5	0.667	1.0	50



For run 1, 2, and 3 $\frac{C_i}{R}$ vs $\frac{1}{m_c}$ plot has intercept = 0

(a) Therefore:

- No resistance to gas absorption and the reaction rate is independent of particle diameter.
- Installing a more efficient sparger will not help the overall reaction rate.
- Increasing stirring rate would not help.

(b) This is the case of reaction rate limited. $\frac{1}{k_c a_c} = 0$, $\eta = 1$

$$\text{slope} = \frac{1}{k} \quad \text{or} \quad k = 0.667 \frac{\text{dm}^3}{\text{min gm cat}}$$

(c) For run 4 slope = 6 = $\frac{1}{k_c a_c} + \frac{1}{\eta k}$

$$\eta = \frac{3}{\phi} = \frac{3}{9} = 0.333$$

$$a_c = \frac{6}{d_p \rho_p} = \frac{6}{(0.075 \text{ cm})(2 \times 10 \text{ g/cm}^3)} = 40 \frac{\text{cm}^2}{\text{gm}} = 0.4 \frac{\text{dm}^2}{\text{gm}} \quad \rho = 2 \text{ g/cm}^3$$

P12-20 cont'd

$$6 \frac{\text{gm min}}{\text{dm}^3} = \frac{1}{0.4 k_c} + \frac{1}{(0.333)(0.667)} = \frac{1}{0.4 k_c} + 4.5$$

$$k_c = \frac{1}{(6 - 4.5) 400} = 1.666 \frac{\text{dm}}{\text{min}}$$

$$r_c = \frac{1}{(k_c a_c)} = \frac{1}{\left(1.666 \frac{\text{dm}}{\text{min}}\right) \left(0.4 \frac{\text{dm}^2}{\text{gm}}\right)} = 1.5 \frac{\text{gm min}}{\text{dm}^3}$$

$$r_{\text{overall}} = (r_{\text{cr}}) \left(\frac{1}{m_c}\right) + r_b = \left(6 \frac{\text{gm min}}{\text{dm}^3}\right) \left(\frac{1 \text{ dm}^3}{2 \text{ gm}}\right) + 0$$

$$r_{\text{overall}} = 3 \text{ min}$$

$$\text{Resistance of external mass-transfer} = \frac{1}{m_c} r_c = \frac{1 \text{ dm}^3}{2 \text{ gm}} \times 1.5 \frac{\text{gm min}}{\text{dm}^3} = 0.75 \text{ min}$$

$$\% \text{ external mass-transfer resistance} = \frac{0.75}{3} \times 100\% = 25\%$$

P12-21

$$r_A = \frac{C_i}{\frac{1}{k_b a_b} + \frac{1}{mk_c a_c} + \frac{1}{mk\eta C_{\text{org}}}}$$

Resistance due to the first term:

$$\frac{1}{k_b a_b} = \frac{1}{0.3 \text{ s}^{-1}} = 3.33 \text{ sec}$$

Resistance due to the first term:

$$a_c = \frac{6}{\rho_p d_p} = \frac{6}{1500 \frac{\text{kg}}{\text{m}^3} (1 \times 10^{-4} \text{ m})} = 40 \frac{\text{m}^2}{\text{kg}}$$

$$m = 0.1 \text{ kg} / \text{m}^3$$

$$\frac{1}{mk_c a_c} = \frac{1}{\left(0.1 \frac{\text{kg}}{\text{m}^3}\right) \left(0.005 \times 10^{-2} \frac{\text{m}}{\text{s}}\right) \left(40 \frac{\text{m}^2}{\text{kg}}\right)} = 5000 \text{ sec}$$

Resistance due to the third term:

$$C_{\text{org}} = C_{\text{org},0} (1 - X)$$

Assuming reaction occurs in well-mixed CSTR and concentration on the surface equals bulk concentration.

P12-21 cont'd

$$C_{org,0} = 2.5 \text{ k mol/m}^3$$

Assume that tortuosity = 1.5 and constriction = 0.8

$$D_0 = D_L \frac{\sigma \epsilon_p}{\tau} = \frac{(10^{-9})(0.8)(0.4)}{(1.5)} = 2.133 \times 10^{-10} \frac{\text{m}^2}{\text{s}}$$

$$\phi = R \sqrt{\frac{k_p C_{org}}{D_c}} = \frac{1 \times 10^{-4}}{2} \text{ m} \sqrt{\frac{0.048 \frac{\text{m}^6}{\text{kg kmol s}} \times 1500 \frac{\text{kg}}{\text{m}^3} \times 2.5 \frac{\text{kmol}}{\text{m}^3} (1-X)}{2.133 \times 10^{-10} \frac{\text{m}^2}{\text{s}}}}$$

$$\phi = 45.93 \sqrt{1-X}$$

$$\eta = \frac{3}{\phi} = \frac{0.065}{\sqrt{1-X}}$$

$$\frac{1}{m\eta k C_{org}} = \frac{1}{\left(0.1 \frac{\text{kg}}{\text{m}^3}\right) \left(\frac{0.065}{\sqrt{1-X}}\right) \left(0.048 \frac{\text{m}^6}{\text{kg kmol s}}\right) \left(2.5 \frac{\text{kmol}}{\text{m}^3}\right) (1-X)}$$

$$\frac{1}{m\eta k C_{org}} = \frac{1282}{\sqrt{1-X}} \text{ sec}$$

$$\text{Let } X = 0.80 \Rightarrow \frac{1}{\mu\eta k C_{org}} = 2867 \text{ sec}$$

Gathering all the resistance terms, at $X = 0.80$

Step	Resistance (sec)	Percent
Gas absorption	3.33	0.04
Transport to catalyst surface	5000	63.53
Internal diffusion & reaction	2867	36.43
Total	7870.33	100%

(b) Assume the system behaving as a batch reactor.

$$\frac{dN_A}{dt} = r_A V$$

$$\text{Rate law: } r_A = \frac{C_i}{\frac{1}{k_b a_b} + \frac{1}{m k_c a_c} + \frac{1}{m k \eta C_A}}$$

$$\begin{aligned} \text{Stoichiometry: } C_A &= C_{A0} (1-X) \\ N_A &= C_A V \end{aligned}$$

12-31

P12-21 cont'd

$$\frac{d}{dt}(C_A V) = r_A V \quad \text{where } V \text{ is constant}$$

$$\frac{dC_A}{dt} = \frac{C_i}{\frac{1}{k_b a_b} + \frac{1}{mk_c a_c} + \frac{1}{mk\eta C_A}}$$

$$\frac{dX}{dt} = \frac{\left(\frac{C_i}{C_{A0}}\right)}{\frac{1}{k_b a_b} + \frac{1}{mk_c a_c} + \frac{1}{mk\eta C_{A0}(1-X)}}$$

$$\frac{dX}{dt} = \frac{\left(\frac{0.01 \text{ kmol/m}^3}{2.5 \text{ kmol/m}^3}\right)}{5.33 + 5000 + \frac{1282}{\sqrt{1-X}}} = \frac{0.004}{5003.33 + \frac{1282}{\sqrt{1-X}}}$$

CDP12-A No solution will be given

CDP12-B No solution will be given

CDP12-C No solution will be given

CDP12-D No solution will be given

CDP12-E No solution will be given

CDP12-F No solution will be given

CDP12-G Part (c) is done first.

(c) Only the gas phase resistances are determined here. The assumption of pseudo first order kinetics means that gas phase resistances are much larger than the liquid phase resistances and are rate controlling. In part (d) where the other assumption is made, liquid phase resistances are determined.

$$r_A = \frac{\frac{C_{H_2}}{H}}{\frac{(1-\epsilon)\rho_p}{Hk_g a_i} + \frac{(1-\epsilon)\rho_p}{k_l a_i} + \frac{1}{k_c a_c} + \frac{1}{\eta k C_{org,s}}}$$

We need to evaluate parameters in the above equation. The first term:

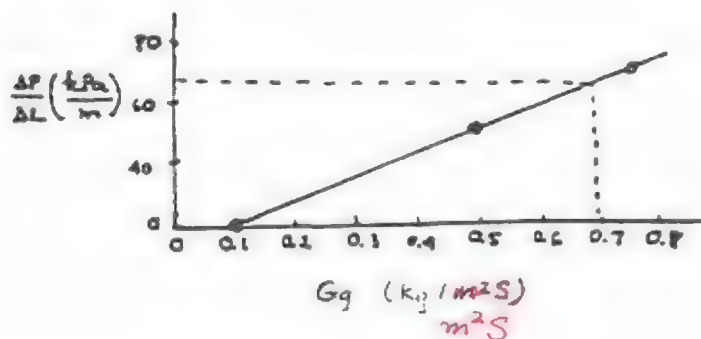
$$k_g a_i = 2 + 0.91 E_g^{2/3} \quad E_g = \frac{\Delta P U_g}{\Delta L}$$

$$v_0 = 36 \frac{\text{mol}}{\text{s}} \times 0.0224 \frac{\text{m}^3}{\text{mol}} \times \frac{1 \text{ atm}}{2 \text{ atm}} \times \frac{400 \text{ K}}{273 \text{ K}} = 0.5907 \frac{\text{m}^3}{\text{s}}$$

$$A_c = \frac{\pi D^2}{4} = \frac{\pi}{4} (1 \text{ m})^2 = 0.785 \text{ m}^2$$

$$U_g = \frac{v_0}{A_c} = \frac{0.5907 \text{ m}^3/\text{s}}{0.785 \text{ m}^2} = 0.7526 \text{ m/s}$$

$$G_g = \frac{m_g}{A_c} = 36 \frac{\text{mol}}{\text{s}} \times \frac{(2+28) \text{ g}}{2 \text{ mol}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{1}{0.785 \text{ m}^2} = 0.69 \frac{\text{kg}}{\text{m}^2 \text{ s}}$$



From the graph above: $\frac{\Delta P}{\Delta L} = 65 \frac{\text{kPa}}{\text{m}}$ at $0.69 \frac{\text{kg}}{\text{m}^2 \text{ s}}$

$$E_g = (65 \frac{\text{kPa}}{\text{m}})(0.7526 \frac{\text{m}}{\text{s}}) = 48.919 \frac{\text{kPa}}{\text{s}} = 1025 \frac{\text{ft lbf}}{\text{ft}^3 \text{ s}}$$

$$k_g a_i = 2 + 0.91 (1025)^{2/3} = 94.53 \text{ s}^{-1}$$

Solubility: $H' = 0.004 \frac{\text{kmol K}}{\text{m}^3 \text{ atm}}$

$$H = \frac{1}{RTH'} = \frac{1}{\frac{0.082 \text{ m}^3 \text{ atm}}{\text{k mol K}} \times 400 \text{ K} \times 0.004 \frac{\text{kmol}}{\text{m}^3 \text{ atm}}} = 7.62$$

$$R_g = \frac{(1 - \epsilon_p) \rho_p}{H (k g a_i)}$$

$$R_g = \frac{(1 - 0.45) \left(1600 \frac{\text{kg}}{\text{m}^3} \right)}{(7.62) (94.53 \text{ s}^{-1})} = 1.22 \frac{\text{kg s}}{\text{m}^3}$$

The second term: $R_1 = \frac{(1 - \epsilon) \rho_p}{k_c a_i}$

$$k_1 a_i = D_L \left[16.8 \frac{R_g^{1/4}}{G_s^{0.22}} S_c^{1/2} \right]$$

$$R_q = \frac{G_L d_p}{\mu_L} = \frac{\left(5 \frac{\text{kg}}{\text{m}^2 \text{ s}} \right) (0.40 \text{ cm}) \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)}{0.0031 \frac{\text{kg}}{\text{m s}}} = 6.45$$

$$G_s = \frac{d_p^3 \rho_L^2 g}{\mu_L^2} = \frac{(0.4 \times 10^{-2} \text{ m})^3 (700 \text{ kg/m}^3)^2 (9.8 \text{ m/s}^2)}{(0.0031 \frac{\text{kg}}{\text{m s}})^2} = 31.980$$

$$S_c = \frac{\mu_L}{\rho_L D_L} = \frac{0.0031 \frac{\text{kg}}{\text{m s}}}{(700 \text{ kg/m}^3) \left(7 \times 10^{-9} \frac{\text{m}^2}{\text{s}} \right)} = 632.65$$

$$k_1 a_i = \left(7 \times 10^{-9} \frac{\text{m}^2}{\text{s}} \right) \left[\frac{(16.8) (6.45)^{1/4} (632.65)^{1/2}}{(31980)^{0.22}} \right] \text{cm}^2 = 4.81 \times 10^{-3} \text{ s}^{-1}$$

$$R_L = \frac{(1 - 0.45) (1600 \text{ kg/m}^3)}{4.81 \times 10^{-3} \text{ s}^{-1}} = 1.8288 \times 10^5 \frac{\text{kg s}}{\text{m}^3}$$

The third term: $R_c = \frac{1}{k_c a_c}$

$$a_c = \frac{6}{\rho_p d_p} = \frac{6}{\left(1600 \frac{\text{kg}}{\text{m}^3} \right) 0.4 \times 10^{-2} \text{ m}} = 0.9375 \frac{\text{m}^2}{\text{kg}}$$

$$\text{Sh} = 0.266 R_q^{1.15} S_c^{1/3} = (0.266) (6.45)^{1.15} (632.65)^{1/3} = 19.5$$

$$Sh = 0.266 Re^{1.15} Sc^{1/3} = (0.266)(6.45)^{1.15} (632.65)^{1/3} =$$

$$19.5 \quad k_c = \frac{Sh D_L}{d_p} = \frac{(19.5)(7 \times 10^{-9} \text{ m}^2/\text{s})}{0.4 \times 10^{-2} \text{ m}} = 3.41 \times 10^{-5} \frac{\text{m}}{\text{s}}$$

$$R_c = \frac{1}{(3.41 \times 10^{-5} \frac{\text{m}}{\text{s}})(0.9375 \frac{\text{m}^2}{\text{kg s}})} = 3.13 \times 10^4 \frac{\text{kg s}}{\text{m}^3}$$

The fourth term: $\frac{1}{\eta k C_{org,s}} = \frac{1}{\eta k}$ where $k = 2.5 \times 10^{-5} \frac{\text{m}^3}{\text{kg s}}$

Assume $\tau = 1.5$, $\sigma = 0.8$

$$D_c = D_c \frac{\sigma \epsilon_p}{\tau}$$

$$\phi = R_p \sqrt{\frac{k p_D}{D_c}} = 2 \times 10^{-3} \sqrt{\frac{(1600)(2.5 \times 10^{-5})(1.5)}{(7 \times 10^{-4})(0.8)(0.45)}} = 9.759; \eta = \frac{3}{\phi} = 0.307$$

$$\frac{1}{\eta k} = \frac{1}{(0.307)(2.5 \times 10^{-5} \frac{\text{m}^3}{\text{kg s}})} = 1.3 \times 10^5 \frac{\text{kg s}}{\text{m}^3}$$

Bringing together the resistance terms:

Step	Resistance $\left(\frac{\text{kg s}}{\text{m}^3}\right)$	Percent resistance
Bulk gas - gas interface	1.222	0
Interface - bulk-liquid	1.8288×10^5	53.1
Bulk-liquid - catalyst surface	3.13×10^4	9.1
Diffusion - reaction in pellet	1.3×10^5	37.8
Total = R_T	3.442×10^5	100%

(a) Calculate catalyst weight:

$$(1 + \epsilon) \ln \frac{1}{1 - X} - \epsilon X = \frac{k_{vg}}{v_0} \left(W - \frac{\beta}{2} W^2 \right) \quad (E - 12-3.7)$$

$$k_{vg} = \frac{1}{H R_T} = \frac{1}{(7.62)(3.442 \times 10^5)} = 3.813 \times 10^{-7} \frac{\text{m}^3}{\text{kg s}}$$

$$\frac{k_{vg}}{v_0} = \frac{3.813 \times 10^{-7}}{0.5907} = 6.455 \times 10^{-7} \text{ kg}^{-1}$$

$$\beta = \frac{\alpha}{A_c P_0 \rho (1 - \epsilon_b)} = \frac{\frac{65}{101.3} \frac{\text{atm}}{\text{m}}}{(0.785 \text{ m}^2)(2 \text{ atm})(1600 \text{ kg/m}^3)(0.6)} = \frac{4.257 \times 10^{-4}}{\text{kg}}$$

Substitution yields:

$$(1 - 0.5) \ln \frac{1}{1 - 0.55} - [(-0.5) 0.55] = 6.455 \times 10^{-7} \left(W - \frac{4.257 \times 10^{-4}}{2} W^2 \right)$$

The equation above yields no solution for W.

(b) If P = 100 atm, then:

$$u_0 = 0.5907 \frac{\text{m}^3}{\text{s}} \left(\frac{2 \text{ atm}}{100 \text{ atm}} \right) = 1.1814 \times 10^{-2} \frac{\text{m}^3}{\text{s}}$$

$$U_g = \frac{1.1814 \times 10^{-2} \frac{\text{m}^3}{\text{s}}}{0.785 \text{ m}^2} = 1.5050 \times 10^{-2} \text{ m/s}$$

$$E_g = \left(65 \frac{\text{kPa}}{\text{m}} \right) (1.5050 \times 10^{-2} \text{ m/s}) = 0.9782 \frac{\text{kPa}}{\text{s}} = 20.50 \frac{\text{ft lbf}}{\text{ft}^3 \text{ s}}$$

$$R_g = \frac{(1 - 0.45)(1600)}{7.62 [2 + (0.91)(20.50)^{2/3}]} = 13.10 \frac{\text{kg s}}{\text{m}^3} \text{ still very small, does not affect } R_T$$

$$\frac{k u_g}{u_0} = \frac{3.813 \times 10^{-7}}{1.1814 \times 10^{-2}} = 3.2275 \times 10^{-5} \text{ kg}^{-1}$$

$$\beta = 4.257 \times 10^{-4} \left(\frac{2}{100} \right) = 8.514 \times 10^{-6} \text{ kg}^{-1}$$

$$(1 - 0.5) \ln \frac{1}{(1 - 0.55)} - [(-0.5) 0.55] = 3.2275 \times 10^{-5} \left(W - \frac{8.514 \times 10^{-6}}{2} W^2 \right)$$

$$W^2 = 2.349 \times 10^5 W + 4.907 \times 10^9 = 0$$

$$W = 23174 \text{ kg}$$

The operating condition is P = 100 atm, T = 400°C

(d) By definition: $-r_A = \frac{(C_{A_g} / H)}{\left[R_3 + \frac{1}{\eta_A k C_{B_s}} \right]} = k_{vg} (C_{A_g})$

$$-r_B = \frac{C_{B_s}}{\left[R_{C_1} + \frac{1}{\eta_B k C_{A_s}} \right]} = k_{ul} C_{B_s}$$

In general, C_{B1} will vary significantly, so that k_{v1} , thus C_{AS} will vary significantly. Hence, k_{v1} will also vary significantly as a function of conversion. C_{A8} will vary significantly only if the pressure drop is significant. The Δp factor α is proportional to $\frac{G^2}{\rho D_p}$ all else constant (assuming turbulent). Between the present case and part (b),

$$G/P = \text{constant}, G^2 / G^1 = 2/15 \text{ (because } \bar{M}_1 = 15, \bar{M}_2 = 2) \text{ and } D_{p2}/D_{p1} = 1/4,$$

$$\text{so } \alpha_2 = \alpha_1 (8/2.5) = 5 \times 10^{-8} \text{ kg}^{-1}. \text{ Assuming a liberal } w = 5 \times 10^4 \text{ kg},$$

$$P_f = P_0 (1 - \alpha w) = 99.75 \text{ atm. Thus, } C_{A8} \text{ is essentially constant.}$$

$$\text{Let } R_3 = R_2 + R_1 + R_{C1}$$

$$-r_A = k C_{AS} C_{B5} = -r_B$$

$$\text{Let } = C_{A1} \frac{C_{A8}}{H}$$

$$k C_{AS} C_{B5} \eta = \frac{C_{A1}}{R_3 + \frac{1}{\eta k C_{B5}}} = \frac{C_{B1}}{R_{C1} + \frac{1}{\eta k C_{AS}}}$$

$$\text{Then, } C_{AS} = \frac{C_{A1}}{[1 - R_3 k \eta C_{B5}]} ; C_{B5} = \frac{C_{B1}}{[1 + R_{C1} k \eta C_{AS}]}$$

$$\text{Let } Q_2 = R_3 k \eta C_{B5}, Q_1 = R_{C1} k \eta C_{AS}, C_A^* = \frac{C_{A1}}{C_{A1}}, C_B^* = \frac{C_{B1}}{C_{B1}}$$

$$C_A^* = \frac{1}{1 + Q_2 / 2 C_B^*}, C_B^* = \frac{1}{1 + Q_1 C_A^*}, C_A^* = \frac{1}{1 - Q_2 \left[\frac{1}{1 + Q_1 C_A^*} \right]}$$

Substituting for C_B^* :

$$C_A^* = \frac{1 + Q_1 C_A^*}{1 + Q_2 + Q_1 C_A^*}$$

$$C_A^* + Q_1 C_A^{*2} + Q_2 C_A^* = 1 + Q_1 C_A^*$$

$$Q_1 C_A^{*2} + (1 + Q_2 - Q_1) C_A^* - 1 = 0$$

This allows C_{AS} to be calculated from C_{A1} , C_{B1} , and constant parameters k, η, R_3, R_{C1} . Given C_{AS} , $-r_B$ can be calculated. For an overall material balance:

$$F_{B0} \frac{dX}{dW} = k_{v1} C_{B0} (1 - X)$$

$$\frac{dX}{dW} = \frac{1}{F_{B_0}} \frac{C_{B_0}(1-X)}{R_{C_2} + \frac{1}{k\eta C_{A_5}(X)}}$$

Where $C_{A_5}(X)$ is C_{A_5} evaluated at $C_{B_1} = C_{B_0}(1-X)$

$$\frac{dX}{dW} = \frac{1}{F_{B_0}} \frac{C_{B_0}(1-X)k\eta C_{A_1} C_A^*}{R_{C_2} k\eta C_{A_1} C_A^* + 1} = \frac{(1-X)(Q_1/R_{C_2}) C_A^*}{Q_1 C_A^* + 1} \frac{C_{B_0}}{F_{B_0}}$$

$$\frac{dX}{dW} = \frac{C_{B_0}}{R_{C_2} F_{B_0}} = \frac{Q_1 C_A^*(X)}{Q_1 C_A^*(X) + 1} (1-X)$$

Let W = total weight, $\omega = \frac{W}{W}$

$$\frac{dX}{dW} = \frac{C_{B_0} W}{F_{B_0} R_{C_2}} = \frac{Q_1 C_A^*(X)}{Q_1 C_A^*(X) + 1} (1-X) = \frac{Q_3 Q_1 C_A^*}{Q_1 C_A^* + 1} (1-X) = \frac{dX}{dW}$$

$$Q_1 = R_{C_2} k\eta C_{A_1}, Q_2 = R_3 k\eta C_{B_0}, Q_3 = \frac{C_{B_0} W}{F_{B_0} R_{C_2}}$$

$$\eta = \frac{3}{\phi^2} (\phi \cosh \phi - 1) \text{ where } \phi = \left[\frac{k\delta^2 (C_{A_5} + C_{B_5})}{D} \right]^{1/2}$$

When $C_{A_5} \gg C_{B_5}$ this becomes correct for pseudo-first-order kinetics in C_{B_5} . Similarly, $C_{B_5} \gg C_{A_5}$ gives η applied to pseudo-first-order kinetics in C_{A_5} . When $C_{A_5} = C_{B_5}$, for large ϕ , this definition of ϕ gives $\frac{1}{\sqrt{2}}$ times the first order η , which is close to the (proper) 2nd order η . So, our definition of ϕ is an approximation, but one which is simple, correct in the limits, and nearly correct in intermediate behavior. Therefore, we must guess η , solve for C_{A_5} , C_{B_5} , calculate a revised η , and recalculate C_{A_5} , C_{B_5} , etc. This introduces two more dimensionless groups, $\frac{k\delta^2 C_{A_1}}{D}$ and $\frac{k\delta^2}{D} C_{B_0}$. Numerically,

$$R_3 = 230811.3 \text{ kg s/m}^3$$

$$R_{C_2} = 19130 \text{ kg s/m}^3$$

$$\delta = 0.5 \times 10^{-3} \text{ m}$$

$$D_H = 7 \times 10^{-9} \text{ m}^2/\text{s}$$

$$D_{org} = 2.5 \times 10^{-9} \text{ m}^2/\text{s}$$

$$k = 9.142857 \times 10^{-6} \frac{\text{m}^6}{\text{kg kmol s}}$$

CDP12-G cont'd

$$C_{B_0} = 2.734 \text{ kmol/m}^3$$

$$C_{A1} = 0.39981 \text{ kmol/m}^3$$

$$F_{B_0} = 1.53398 \times 10^{-2} \text{ kmol/s}$$

$$\tau = 1.5$$

$$\sigma = 0.8$$

$$\epsilon_p = 0.45$$

$$\rho_C = 1600 \text{ kg/m}^3$$

$$Q_1 = R_C; k C_{A1} (19130) (9.142857 \times 10^{-6}) (0.39981) = 6.9927 \times 10^{-2}$$

$$Q_2 = R_3; k C_{B_0} (230811.3) (9.142857 \times 10^{-6}) (2.734) = 5.7695$$

$$Q_3 = \frac{k \delta^2 C_{A1} \tau \rho_C}{D_H \sigma \epsilon_p} = \frac{(9.142857 \times 10^{-6}) (5 \times 10^{-4})^2 (0.39981) (1.5) (1600)}{(7 \times 10^{-9}) (0.8) (0.45)} = 0.87033$$

$$Q_4 = \frac{k \delta^2 C_{B_0} \tau \rho_C}{D_{org} \sigma \epsilon_p} = \frac{(9.142857 \times 10^{-6}) (5 \times 10^{-4})^2 (2.734) (1.5) (1600)}{(2.5 \times 10^{-9}) (0.8) (0.45)} = 16.664$$

$$Q_5 = \frac{C_{B_0} W}{F_{B_0} R_{C1}} = \frac{(2.734) W}{(1.53398 \times 10^{-2}) (1.9130)} = (9.3167 \times 10^{-3} \text{ kg}^{-1}) (W \text{ kg})$$

Using the constants in a computer program to solve for W, we get $W = 18450 \text{ kg catalyst}$. Note that the 18450 is wrong due to complete error. Also, the D's in Q_3 and Q_4 should be switched. Thus:

$$Q_3 = \frac{k \delta^2 C_{A1} \tau \rho_C}{D_{org} \sigma \epsilon_p} = 2.4369$$

$$Q_4 = \frac{k \delta^2 C_{B_0} \tau \rho_C}{D_H \sigma \epsilon_p} = 5.9514$$

This results in $W = 14021.38 \text{ kg}$. If you assume $C_{A5} = C_{A1}$ and $C_5 \gg C_A$ to calculate a constant k_{ol} and solve for $W = \frac{F_{B_0}}{C_{B_0} k_{ol}} \ln \left(\frac{1}{1-X} \right)$, one gets $W = 6523.4 \text{ kg}$. If one assumes $C_B \gg C_A$ but $C_{A5} = 0.1927 C_{A1}$, then one gets $W = 32372.4 \text{ kg}$. These results show that it is necessary to consider the coupling.

12-40

0127
 Enter G1, G2, G3, G5, G7,
 6.9928E-02, 5.7695, 1.4369, 5.9514, 9.3167E-07
 Enter WT (Kg) and NDIV.
 15000., 5
 File name missing or blank - Please enter name
 UNIT 77 out

W	X	CAS	CBS	Eta
.0	.0000000	.1927036	.9902159	.7552484
.1	.1351785	.2117485	.9889556	.7545540
.2	.2667385	.2356787	.9872675	.7765590
.3	.3936997	.2664159	.9855566	.7988025
.4	.5146849	.3067951	.9826897	.8210852
.5	.6277359	.3608770	.9791958	.8420044
.6	.7301055	.4338495	.9745791	.8597715
.7	.8181756	.5301071	.9686815	.8721856
.8	.8880618	.6471415	.9617977	.8777192
.9	.9374682	.7678755	.9550111	.8775130
1.0	.9679469	.8668925	.9496692	.8742695

Another try ?
 Y
 Enter WT (Kg) and NDIV.
 14021.08, 10

W	X	CAS	CBS	Eta
.0	.0000000	.1927036	.9902159	.7552484
.1	.1264608	.2105758	.9890447	.7552948
.2	.2498087	.2322189	.9875965	.7754229
.3	.3692705	.2597456	.9857763	.7943914
.4	.4837854	.2951245	.9834518	.8155458
.5	.5918802	.3414229	.9804440	.8354571
.6	.6915176	.4026897	.9765547	.8555507
.7	.7799845	.4831501	.9715514	.8675158
.8	.8540641	.5841506	.9654655	.8757046
.9	.9109537	.6980175	.9589001	.8781119
1.0	.9500000	.8038501	.9529595	.8765705

Another try ?
 N
 Stop - Program terminated.
 C:\calc\5287

(e) Plug flow model works $\frac{L}{d_p} > \frac{20}{P_e} n \ln\left(\frac{1}{1-X}\right)$

$$L = 1235 \text{ kg} \frac{\text{m}^3}{1600 \text{ kg}} \left(\frac{1}{0.785 \text{ m}^2} \right) = 0.98 \text{ m}$$

$$U_c = \frac{5 \text{ kg/m}^2 \text{ s}}{700 \text{ kg/m}^3} = 0.007143 \frac{\text{m}}{\text{s}}$$

$$P_e = \frac{U_c d_p}{D_{AX}} = \frac{(0.007143 \frac{\text{m}}{\text{s}})(0.1 \times 10^{-2} \text{ m})}{0.38 \times 10^{-4} \frac{\text{m}^2}{\text{s}}} = 0.188$$

$$\frac{L}{d_p} = \frac{0.98 \text{ m}}{0.1 \times 10^{-2} \text{ m}} = 980$$

CDP12-G cont'd

$$\frac{20}{P_e} n \ln \frac{1}{1-X} = \frac{20}{0.188} \ln \frac{1}{1-0.95} = 318.7$$

Yes, plug flow model is a good assumption.

CDP12-H No solution will be given**CDP12-I** No solution will be given**CDP12-J** Part (b) is done first.

(b) Let B = organic. Then the liquid phase resistance is:

$$-r_B = \frac{1}{\frac{1}{k_C a_C} + \frac{1}{\eta k C_{H_2S}}} C_B$$

The first term:

$$a_C = \frac{6}{p_p d_p} = \frac{6}{\left(1500 \frac{\text{kg}}{\text{m}^3}\right) \left(1/8 \ln \left(\frac{254 \times 10^{-2} \text{ m}}{1 \text{ m}}\right)\right)} = \frac{6}{\left(1500 \frac{\text{kg}}{\text{m}^3}\right) (3.175 \times 10^{-3} \text{ m})}$$

$$a_C = 1.260 \frac{\text{m}^2}{\text{kg}}$$

$$Sh = 0.266 Re_L^{1.15} Sc^{1/3}$$

$$Re_L = \frac{G_L d_p}{\mu_L} = \frac{(8 \text{ kg/m}^2 \text{ s})(3.175 \times 10^{-3} \text{ m})}{3.0 \times 10^{-3} \text{ kg/m s}} = 8.47$$

$$Sc = \frac{\mu}{\rho D_{AB}} = \frac{(3 \times 10^{-3} \text{ kg/m s})}{(900 \text{ kg/m}^3) 6 \times 10^{-11} \text{ m}^2/\text{s}} = 55555$$

$$Sh = (0.266)(8.47)^{1.15} (55,555)^{1/3} = 118.45 = \frac{k_C d_p \alpha}{D_L}$$

$$k_C = \frac{(118.45) 6 \times 10^{-11} \text{ m}^2/\text{s}}{3.175 \times 10^{-3} \text{ m}} = 2.238 \times 10^{-6} \text{ m/s (assuming } \alpha = 1)$$

$$\frac{1}{k_C a_C} = \left[(2.238 \times 10^{-6} \text{ m/s}) (1.260 \text{ m}^2/\text{kg}) \right]^{-1} = 3.546 \times 10^5 \text{ kg s/m}^3$$

The second term:
$$\frac{n_{H_2}}{n_{N_2}} = \frac{\frac{0.2 \text{ kg/m}^2 \text{ s}}{2 \text{ g/gmol}}}{\frac{0.05 \text{ kg/m}^2 \text{ s}}{2.8 \text{ g/gmol}}} = 5.6$$

12-42

CDP12-I cont'd

$$y_{H_2} = \frac{n_{H_2}}{n_{H_2} + n_{N_2}} = \frac{1}{1 + \frac{n_{N_2}}{n_{H_2}}} = \frac{1}{1 + \frac{1}{5.6}} = 0.85$$

$$P_{H_2} = (50 \text{ atm})(0.85) = 42.5 \text{ atm}$$

$$C_{H_2S} = (42.5 \text{ atm}) \left(0.0068 \frac{\text{mol}}{\text{dm}^3 \text{ atm}} \right) = 0.289 \frac{\text{g mol } H_2}{\text{dm}^3 \text{ liquid}}$$

$$k' = k_{CH_2S} = \left(2 \times 10^{-5} \frac{\text{m}^6}{\text{k mol kg s}} \right) \left(0.289 \frac{\text{k mol}}{\text{m}^3} \right) = 5.78 \times 10^{-6} \frac{\text{m}^3}{\text{kg s}}$$

$$D_e = D_L \frac{\sigma_{e_0}}{\tau} = \left(6 \times 10^{-11} \frac{\text{m}^2}{\text{s}} \right) \frac{(0.8)(0.5)}{(3.8)} = 6.316 \times 10^{-12} \frac{\text{m}^2}{\text{s}}$$

$$\phi = R \sqrt{\frac{k' \rho_p}{D_e}} = \frac{3.175 \times 10^{-3}}{2} \sqrt{\frac{(5.78 \times 10^{-6}) 1500}{6.316 \times 10^{-12}}} = 58.8$$

$$\eta = \frac{3}{\phi} = 0.051$$

$$\frac{1}{\eta k_{CH_2S}} = \frac{1}{\eta k'} = \frac{1}{(0.051)(5.78 \times 10^{-6})} = 3.392 \times 10^6 \text{ kg s/m}^3$$

Liquid Resistance

Step	Resistance	Percent
Bulk liquid to catalyst surface	3.546×10^5	9.5
Diffusion/reaction	3.392×10^6	90.5
Total	3.746×10^6	100%

$$\text{Gas phase resistance: } -r_A = \frac{1/H}{\frac{(1-\epsilon)\rho_p}{H \text{ kg } a_i} + \frac{(1-\epsilon)\rho_p}{k_l a_i} + \frac{1}{k_l a_c} + \frac{1}{\eta k C_{org,s}}} C_{H_2} \text{ (gas)}$$

$$\text{The first term: } \text{kg } a_i = 2 + 0.91 E_G^{2/3}$$

$$E_G = \frac{\Delta P}{\Delta L} U_g$$

CDP12-1 cont'd

Assuming ideal gas behavior:

$$\rho_g = \frac{PM}{RT} = \frac{50(2)}{0.082(373)} = 3.2695 \frac{\text{kg}}{\text{m}^3}$$

$$U_g = \frac{G_g}{\rho_g} = \frac{0.2 \text{ kg/m}^2 \text{ s}}{3.2695 \text{ kg/m}^3} = 0.06117 \frac{\text{m}}{\text{s}}$$

$$E_g = \left(30 \frac{\text{kPa}}{\text{m}}\right) (0.06117 \frac{\text{m}}{\text{s}}) = 1.8352 \frac{\text{kPa}}{\text{s}} = 38.46 \frac{\text{ft lbf}}{\text{ft}^3 \text{ s}}$$

$$k_g a_i = 2 + 0.91 (38.46)^{2/3} = 12.37 \text{ s}^{-1}$$

$$H = \frac{1}{RTH} = \frac{1}{\frac{0.082 \text{ m}^3 \text{ atm}}{\text{k mol K}} (373 \text{ K}) \frac{0.0068 \text{ kmol}}{\text{m}^3 \text{ atm}}} = 4.81$$

$$\frac{(1-\epsilon) \rho_p}{H k_g a_i} = \frac{(0.5)(1500 \text{ kg/m}^3)}{(4.81)(12.37 \text{ s}^{-1})} = 12.605 \frac{\text{kg s}}{\text{m}^3}$$

The second term: $\frac{k_1 a_i}{D_L} = 16.8 \frac{R_e^{1/4}}{G_s^{0.22}} S_C^{1/2}$

$$S_C = \frac{\mu_L}{\rho_L D_{H_2}} = \frac{0.0031 \text{ kg/m s}}{(900 \text{ kg/m}^3)(8 \times 10^{-9} \text{ m}^2/\text{s})} = 430.56$$

$$G_s = \frac{d_p^3 \rho_L^2 g}{\mu_L^2} = \frac{(3.175 \times 10^{-3} \text{ m})^2 (900 \text{ kg/m}^3)^2 (9.8 \text{ m/s}^2)}{(0.0031 \text{ kg/m s})^2} = 2.6437 \times 10^4$$

$$\frac{k_1 a_i}{D_{H_2}} = (16.8) \frac{(8.47)^{1/4} (430.56)^{1/2}}{(2.6437 \times 10^4)^{0.22}} = 63.30$$

$$k_1 a_i = 63.30 (8 \times 10^{-7}) = 5.064 \times 10^{-5} \text{ sec}^{-1}$$

$$\frac{(1-\epsilon) \rho_p}{k_1 a_i} = \frac{(0.5)(1500 \text{ kg/m}^3)}{5.064 \times 10^{-5} \text{ s}^{-1}} = 1.481 \times 10^7 \frac{\text{kg s}}{\text{m}^3}$$

The third term:

$$Sh' = 0.266 R_e^{1.15} S_C^{1/3} = 0.266 (8.47)^{1.15} (430.56)^{1/3} = 23.44$$

$$23.44 = \frac{k_C d_p}{D_{H_2}} \propto \text{Assuming } \alpha = 1.0$$

CDP12-1 cont'd

$$k_c = \frac{(23.44)(8 \times 10^{-9})}{3.175 \times 10^{-3}} = 5.906 \times 10^{-5} \text{ m/s}$$

$$k_c a_c = (5.906 \times 10^{-5} \text{ m/s})(1.260 \text{ m}^2/\text{kg}) = 7.442 \times 10^{-5} \text{ m}^3/\text{kg s}$$

$$\frac{1}{k_c a_c} = 1.344 \times 10^4 \text{ kg s/m}^3$$

The last term:

$$\frac{1}{\eta k C_{org}} = \frac{1}{(0.051) \left(2 \times 10^{-5} \frac{\text{m}^3}{\text{kmol kg s}} \right) \left(0.07 \frac{\text{kmol}}{\text{m}^3} \right)} = 1.40 \times 10^7 \frac{\text{kg s}}{\text{m}^3}$$

Gathering up the resistances in gas phase:

Step	Resistance	Percent
Bulk gas - gas interface	12.605	0.0
Interface - bulk liquid	1.481×10^7	51.4
Bulk liquid - catalyst surface	1.344×10^4	0.0
Diffusion - reaction in peller	1.40×10^7	48.6
Total	2.882×10^7	100%

(a) Mole balance, plug flow model: $-\frac{dF_B}{dW} = -r_B$

Rate Law: $r_B = k_{vl} C_B$

Stoichiometry: $C_B = C_{B0}(1 - X_B)$

Combine: $\frac{dX_B}{dW} = \frac{C_{B0}}{F_{B0}} k_{vl} (1 - X_B)$

$$\frac{dX_B}{1 - X_B} = \frac{C_{B0}}{F_{B0}} k_{vl} dW$$

$$k_{vl} = \frac{1}{R_T} = \frac{1}{3.746 \times 10^6} = 2.67 \times 10^{-7} \frac{\text{m}^3}{\text{kg s}}$$

$$C_{B0} = 0.07 \frac{\text{kmol}}{\text{m}^3}$$

12-45

CDP12-1

$$F_{B0} = \frac{\text{cont'd} \quad (8 \text{ kg/m}^2 \text{ s}) \frac{\pi}{4} (1 \text{ m})^2}{(900 \text{ kg/m}^3) \left(0.07 \frac{\text{kmol}}{\text{m}^3}\right)} = 9.973 \times 10^{-2} \frac{\text{kmol}}{\text{s}}$$

$$\frac{dX_B}{(1 - X_B)} = \frac{\left(0.07 \frac{\text{kmol}}{\text{m}^3}\right)}{9.973 \times 10^{-2} \frac{\text{kmol}}{\text{s}}} \left(2.67 \times 10^{-7} \frac{\text{m}^3}{\text{kg s}} dW\right) \quad W \text{ in kgs}$$

$$\frac{dX_B}{(1 - X_B)} = 1.874 \times 10^{-7} dW$$

$$\ln \frac{1}{(1 - X_B)} = 1.874 \times 10^{-7} W$$

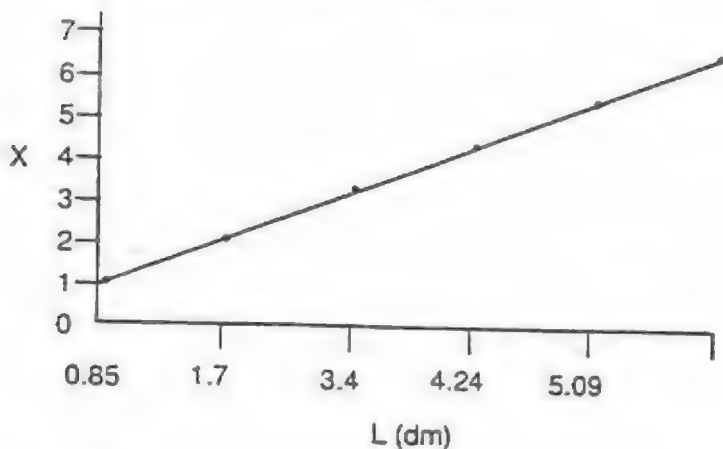
$$W_{\max} = \left\{ \frac{\pi}{4} (1 \text{ m})^2 \right\} (6 \text{ m}) 0.5 \left(1500 \frac{\text{kg}}{\text{m}^3} \right) = 3534 \text{ kg}$$

$$\ln \frac{1}{(1 - X_{B \max})} = 6.623 \times 10^{-4}$$

$$X_{B \max} = 6.621 \times 10^{-4}$$

This choice of η and k gives a rather low total conversion. Since diffusion-reaction resistance is the largest by far, W coefficient is almost linear in it.

W (kg)	L (m)	X_R
500	0.85	9.369×10^{-5}
1000	1.70	1.874×10^{-4}
1500	2.55	2.811×10^{-4}
2000	3.40	3.747×10^{-4}
2500	4.24	4.684×10^{-4}
3000	5.09	5.620×10^{-4}
3500	5.94	6.557×10^{-4}



(c) For all the conditions used in this problem, the diffusion into pellet and reaction resistances were dominate for both liquid and gas.

At 50 atm total pressure with 80% H_2 in the gas feed. The equilibrium H_2 solubility is 0.289 gmol/l vs organic maximum concentration of 0.07 gmol/l. Also, the molar flow rate of H_2 is higher than the flow rate of organics.

For these reasons, curing gas flow rate could have no effect on the conversion provided the same inlet pressure is maintained. There will still be a huge excess of the H_2 and the system will behave as a quasi first-order reaction modeled as a plug flow reactor. The H_2 concentration at all points will be essentially the equilibrium saturation liquid concentration.

Answer. No change in conversion.

- a) The Orcutt model agrees with Kunii-Levenspeil in believing all the bubbles are uniform throughout the reactor and both also agree that transfer from bubble phase to emulsion phase is by two superimposed independent mechanisms. However they differ in that in K-L believes that transfer from emulsion and cloud-wake is different from Orcutt's belief is the same as bubble to emulsion transfer. A disadvantage of the Orcutt model is that the mass transfer parameter is over estimated making the model incorrect

The Rowe and Partridge model assumes that bubble size changes as well as the velocities which K-L does not do. However due to the model they used, the cloud area gets overestimated and does not correlate to the bed cross-sectional area.

The Kato and Wen model assumes that the bubble phase includes clouds and voids. K-L only includes clouds. It also assumes that each phase is perfectly mixed which K-L also agrees with. But interphase transfer uses a different mechanism. This model gives the lowest F factor, but the dense phase profile and outlet reactant concentrations were over predicted.

$$b) K_{ce} = \frac{6.4}{D_p} = \frac{6.4}{4.87} = 1.31$$

Solving for K_R :

$$K_R = 0.01 + \frac{1}{0.017 + \frac{1}{0.187 + \frac{1}{\frac{1}{2.28} + 0.065}}} = 2.11$$

Then finding the conversion:

$$X = 1 - \exp\left(-\frac{K_R k_{cor} h}{U_b}\right) = 0.18$$

a)

$$\langle \varepsilon_B \rangle = 5.4 * 10^{-2} (U - U_{mf})^{0.4} = 0.11$$

$$D_B = 5.3 * 10^{-3} U y + 2.1$$

At a height of $y = 0.5H$

$$y = 30 \text{ cm.}$$

$$D_B = 3.4 \text{ cm}$$

$$f = 1.15 * 10^3 \langle \varepsilon_B \rangle D_B^{-1.45} = 21.7$$

$$U_B = 13 * A_B^{0.35}$$

$$A_B = \frac{\pi D_B^2}{4} = 6.74 \text{ cm}^2$$

$$U_B = 25.4 \text{ cm}$$

b) We now must find the conversion:

$$K_{ce} = 6.77 \left(\frac{\varepsilon_{mf} D_{AB} U_B}{D_B^2} \right)^{0.5} = 0.89$$

$$K_{bc} = 4.5 \left(\frac{1.48}{3.4} \right) + 5.85 \left(\frac{D_{AB}^{0.5} g^{0.25}}{D_B^{1.25}} \right) = 7.5$$

$$\gamma_c = (1 - \varepsilon_{mf}) \left[\frac{3(\mu_{mf} / \varepsilon_{mf})}{u_b - (\mu_{mf} / \varepsilon_{mf})} + \alpha \right] = 0.24$$

$$\delta = \frac{u - u_{mf}}{u_b - u_{mf} (1 + \alpha)} = 0.28$$

$$\gamma_e = (1 - \varepsilon_{mf}) \frac{1 - \delta}{\delta} - \gamma_c - \gamma_b = 0.632$$

$$K_R = \gamma_b + \frac{1}{\frac{k_{cat}}{K_{bc}} + \frac{1}{\gamma_c + \frac{1}{\frac{1}{\gamma_e} + \frac{k_{cat}}{K_{ec}}}}} = 0.48$$

$$X = 1 - \exp \left(- \frac{K_R k_{cat} h}{U_b} \right) = 0.093$$

Much smaller than that obtained in the example.

CDP12-M

$$u_{mf} = \frac{(\psi d_p)^2 \eta \epsilon_{mf}^2}{150 \mu (1 - \epsilon_{mf})}$$

$$\frac{u_{mf2}}{u_{mf1}} = \frac{\mu_1}{\mu_2} = \left(\frac{T_1}{T_2} \right)^{1/2}$$

Since $\mu_{gas} \propto T^{1/2}$

$$\frac{u_{mf2}}{u_{mf1}} = \left(\frac{273}{546} \right)^{1/2} = \left(\frac{1}{2} \right)^{1/2} = \frac{1}{1.4}$$

The minimum fluidization velocity will decrease by a factor of 1.4 (b)(b).

CDP12-N

Start with the equation for the rate law:

$$-r_A = \Omega k C_{Ae} \quad \text{at top}$$

Then find the concentrations

$$C_{A0} = y_{A0} \frac{P_0}{RT_0} = .1 \frac{\frac{840}{760}}{82.06 * 523} = 2.575 * 10^{-6} \frac{\text{gmol}}{\text{cc}}$$

$$C_{Ae} = 0.939 * C_{Ac} = 0.939(0.961 * C_{Ab})$$

At top

$$C_{Ab} = 0.8 * C_{A0}$$

$$C_{Ae} = (0.939)(0.961)(0.8)2.575 * 10^{-6}$$

$$C_{Ae} = 1.859 * 10^{-6} \frac{\text{gmol}}{\text{cc}}$$

$$\Omega = 2.28$$

Finding the rate:

$$-r_A = 2.28 \frac{\text{cc of cat}}{\text{cc of bubble}} * 0.0858 \frac{\text{cc of gas}}{\text{cc of cat sec}} * 1.859 * 10^{-6} \frac{\text{gmol}}{\text{cc}}$$

$$-r_A = 3.64 * 10^{-7} \frac{\text{gmol}}{\text{cc of bubbles * sec}}$$

CDP12-Q

- a) Assume a ψ of 0.6 and then find ϵ_{mf} .

$$\epsilon_{mf} = \left(\frac{0.071}{\psi} \right)^{1/3} = 0.49$$

Next find the equation for the diameter of the particle and another for the porosity.

$$d_p = \sqrt[3]{\frac{150u_{mf}\mu(1-\epsilon_{mf})}{0.36\eta\epsilon_{mf}^3}}$$
$$\epsilon_{mf} = \frac{0.586 * \mu^{0.058} * d_p^{0.087}}{0.6^{0.7} \rho_s^{0.008} \eta^{0.029} \rho_c^{0.021}}$$

Assume 290K and 760 mmHg: $\mu = 1.89 * 10^{-4}$ cp; $\rho_c = 0.001204$ g/cm³.

Guess a value for the density of the catalyst and plug into the equations for d_p and ϵ_{mf} until $\epsilon_{mf} = 0.5$

$$d_p = 0.27 \text{ cm}$$

- b) Find the diameter of the column:

$$A_c = 314.16 = \pi r^2$$

$$r = 10 \text{ cm}$$

$$D = 20 \text{ cm}$$

Find the maximum and minimum diameters of the bubbles:

$$d_{bm} = 0.652(314.16(10-2))^{0.4} = 14.9$$

$$d_{b0} = 0.00376(8)^2 = 0.24$$

Find the height of the column:

$$\frac{d_{bm} - d_b}{d_{bm} - d_{b0}} = e^{-0.34h/D}$$

$$h = 73 \text{ cm}$$

12-51

CDP12-Q cont'dc) Find u_b

$$0.106 = \frac{10 - 2}{u_b - 2.8}$$

$$u_b = 78.3 \text{ cm/s}$$

Then find the conversion achieved at the height of the tower.

$$73 = \frac{78.3}{k_{cat} K_R} \ln \frac{1}{1 - X}$$

$$X = 0.26$$

CDP12-P

$$h = \frac{U_b}{k_{cat} K_e} \ln \frac{1}{1 - X}$$

$$\frac{h_2}{h_1} = \frac{U_{b2}}{U_{b1}} \frac{K_{R1}}{K_{R2}} \frac{\ln \frac{1}{1 - X_2}}{\ln \frac{1}{1 - X_1}}$$

$$h_2 = h_1$$

$$\varepsilon_{mf2} \equiv \varepsilon_{mf1}$$

$$u_{01} = 2u_{mf1}$$

$$u_{02} = 2u_{01} = 4u_{mf1}$$

a) For reaction limitation

$$K_R \approx (1 - \varepsilon_{mf}) \frac{u_b}{u_0 - u_{mf}}$$

$$1 = \frac{(u_0 - u_{mf})_2 \ln \frac{1}{1 - X}}{(u_0 - u_{mf})_1 \cdot 1.0}$$

$$u_{mf2} = u_{mf1} \left(\frac{1}{2} \right)^2$$

$$u_{mf2} = \frac{1}{4} u_{mf1}$$

$$\ln \frac{1}{1 - X} = \frac{(u_0 - u_{mf})_2}{(u_0 - u_{mf})_1} = \frac{2u_{mf1} - u_{mf1}}{4u_{mf1} - \frac{1}{4}u_{mf1}} = \frac{1}{3.75}$$

$$X_2 = 0.23$$

12-52

CDP12-P cont'd

b) For mass transfer

$$K_R = \frac{K_{bc}}{k_{cat}}$$

$$K_{bc} \equiv 4.5 \frac{u_{mf}}{d_b}$$

$$\frac{h_2}{h_1} = \left(\frac{d_{b2}}{d_{b1}} \right)^{3/2} \frac{u_{mf1}}{u_{mf2}} \frac{\ln \frac{1}{1-X}}{\ln \frac{1}{1-X}}$$

$$d_b \propto (u_0 - u_{mf})^{0.4}$$

$$\ln \frac{1}{1-X_2} = \left(\frac{u_{mf2}}{u_{mf1}} \right) \left(\frac{[u_0 - u_{mf}]_1}{[u_0 - u_{mf}]_2} \right)^{0.6}$$

$$= \frac{1}{4} \frac{u_{mf1}}{u_{mf2}} \left[\frac{u_{mf1}}{3.75 u_{mf1}} \right]^{0.6} = \frac{.45}{4}$$

$$X_2 = 0.11$$

CDP12-Q

$$h = \frac{U_b}{k_{cat} K_R} \ln \frac{1}{1-X}$$

$$\frac{h_2}{h_1} = \frac{U_{b2}}{U_{b1}} \frac{k_{cat1}}{k_{cat2}} \frac{K_{R1}}{K_{R2}}$$

a) For mass transfer:

$$\frac{\varepsilon_{mf2}}{\varepsilon_{mf1}} = \left(\frac{\mu_2}{\mu_1} \right)^{0.058} \left(\frac{\rho_{g1}}{\rho_{g2}} \right)^{0.029} \left(\frac{\eta_1}{\eta_2} \right)^{0.029} \left(\frac{\rho_{g2}}{\rho_{g1}} \right)^{0.021}$$

$$\text{Assume } \eta_1 = \eta_2$$

$$\frac{\varepsilon_{mf2}}{\varepsilon_{mf1}} = \left[\left(\frac{T_2}{T_1} \right)^{1/2} \right]^{0.058} \left(\frac{T_2}{T_1} \right)^{0.029} \left(\frac{T_1}{T_2} \right)^{0.021} = 0.988$$

$$\frac{u_{mf2}}{u_{mf1}} = \frac{\mu_1}{\mu_2} \left(\frac{\varepsilon_{mf2}}{\varepsilon_{mf1}} \right)^3 \frac{1 - \varepsilon_{mf1}}{1 - \varepsilon_{mf2}} = 1.13$$

CDP12-Q cont'd

Now the mass transfer coefficient:

$$K_R = \frac{K_{bc}}{k_{cat}}$$

$$K_{bc} \cong 4.5 \frac{u_{mf}}{d_b}$$

$$d_b \propto (u_0 - u_{mf})^{0.4}$$

$$\frac{h_2}{h_1} = \left(\frac{[u_0 - u_{mf}]_1}{[u_0 - u_{mf}]_2} \right)^{0.6} \frac{u_{mf2}}{u_{mf1}} = \left(\frac{u_{mf1}}{1.13u_{mf1}} \right)^{0.6} \frac{1.13u_{mf1}}{u_{mf1}}$$

$$\frac{h_2}{h_1} = 1.05$$

b) Reaction rate limited:

$$\frac{h_2}{h_1} = \frac{k_{cat1}}{k_{cat2}}$$

$$k_{cat2} = k_{cat1} * \exp \left[\frac{19870}{1.987} \left(\frac{1}{700} - \frac{1}{500} \right) \right] = 0.0033 k_{cat1}$$

$$\frac{h_2}{h_1} = \frac{1}{0.0033} = 303.2$$

CDP12-R

We first need the viscosity and density of the gas which is said to have air-like properties so looking up the two values at this temperature and atmospheric pressure we find that:

$$\mu = 215.39 * 10^{-6} \text{ g/cm} \cdot \text{s}$$

$$\rho = 9.5 * 10^{-4} \text{ g/cm}^3$$

b) We must find η

$$\eta = g(\rho_c - \rho_s) = 980(2 - 9.5 * 10^{-4}) = 1959.069$$

We can then find ϵ_{mf}

$$\epsilon_{mf} = 0.586 * (0.6)^{-0.72} \left(\frac{(215.39 * 10^{-6})^2}{(9.5 * 10^{-6}) 1959.069 (0.01)^3} \right)^{0.029} \left(\frac{9.5 * 10^{-4}}{2} \right)^{0.021}$$

$$\epsilon_{mf} = 0.648$$

12-54

CDP12-R cont'd

a) We can then find u_{mf}

$$\begin{aligned}
 u_{mf} &= \frac{(\psi d_p)^2}{150\mu} \eta \frac{\varepsilon_{mf}^3}{1 - \varepsilon_{mf}} \\
 &= \frac{(0.6 * 0.01)^2}{150 * 215.39 * 10^{-6}} * 1959.069 * \frac{0.648^3}{1 - 0.648} \\
 &\doteq 1.69 \text{ cm/s}
 \end{aligned}$$

c) The diameter of the bed:

$$5 * 1.69 = \frac{2277 * 4}{\pi * D_t^2}$$

$$D_t = 18.6 \text{ cm}$$

d) By trial and error we have to determine what the entrainment velocity is:

$$\begin{aligned}
 u_t &= \frac{\eta d_p^2}{18\mu} = \frac{1959.069 * 0.01^2}{18 * 215.39 * 10^{-6}} = 50 \text{ cm/s} \\
 \text{Re} &= \frac{\rho u_o D}{\mu} = 2.2
 \end{aligned}$$

This is not correct because the Reynold's number is > 0.4 .

$$\begin{aligned}
 u_t &= \left(\frac{1.78 * 10^{-2} \eta^2}{\rho_s \mu} \right)^{1/3} d_p = 69.4 \\
 \text{Re} &= 3.06
 \end{aligned}$$

This is correct because $0.4 < \text{Re} < 500$.

e) Minimum bubble diameter:

$$d_{b0} = 0.00376 (u_0 - u_{mf})^2 = 3.24 \text{ cm}$$

12-55

CDP12-R cont'd

f) Maximum bubble diameter:

$$d_{bm} = 0.652 \left[A_c (u_0 - u_{mf}) \right]^{0.4} = 13.1 \text{ cm}$$

g) Bubble velocity

Guess a bubble diameter of 12.7 cm.

$$u_b = u_0 - u_{mf} + (0.71)(gd_p)^{1/2} = 85.9 \text{ cm/s}$$

h) No solution will be given

i) Fraction of the bed occupied by the bubble:

$$\delta = \frac{u_0 - u_{mf}}{u_b - u_{mf}(1 + \alpha)} = 0.080$$

j) Fraction of the bed occupied by the wake:

$$\alpha\delta = 0.032$$

k) Velocity of the solids:

$$u_s = \frac{\alpha\delta u_b}{1 - \delta - \alpha\delta} = \frac{(0.032)(85.9)}{1 - 0.08 - 0.032} = 3.09 \text{ cm/s}$$

l) Velocity of the rise in the emulsion phase:

$$u_e = \frac{u_{mf}}{\varepsilon_{mf}} - u_s = \frac{1.67}{0.648} - 3.13 = -0.55 \text{ cm/s}$$

m) I can't come up with the final equation

n) K_{BC}

$$K_{BC} = 4.5 \left(\frac{u_{mf}}{d_b} \right) + 5.85 \left(\frac{D_{AB}^{0.5} g^{0.25}}{d_b^{1.25}} \right) = 1.45$$

12-56

o) K_{ce}

$$K_{ce} = 6.77 \left(\frac{\epsilon_{mf} D_{AB} u_b}{d_b^3} \right)^{0.5} = 0.71$$

p) γ_c

$$\gamma_c = (1 - \epsilon_{mf}) \left[\frac{3(u_{mf} / \epsilon_{mf})}{u_b - (u_{mf} / \epsilon_{mf})} + \alpha \right] = 0.15$$

 γ_c

$$\gamma_r = (1 - \epsilon_{mf}) \frac{1 - \delta}{\delta} - \gamma_c - \gamma_b = 3.89$$

q) K_R

$$K_R = \gamma_b + \frac{1}{\frac{k_{cat}}{K_{bc}} + \frac{1}{\gamma_c + \frac{1}{\frac{1}{\gamma_e} + \frac{k_{cat}}{K_{ce}}}}} = 0.15$$

r) Find the necessary concentration to give 90% conversion

$$0.9 = \frac{0.5 - C_A}{0.5}$$

$$C_A = 0.05$$

Solving the differential equation:

$$\frac{dC_{Ab}}{C_{Ab}} = -k_{cat} K_R dt$$

$$\ln C_{Ab} \Big|_{0.5}^{0.05} = -(5 * 0.15) * t \Big|_0^t$$

$$t = 3.07s$$

12-57

CDP12-R cont'd

Solve for the height:

$$h = tu_b = 3.07 * 85.9 = 263.7 \text{ cm}$$

s) The catalyst weight is then:

$$W = \rho_c A_c h (1 - \varepsilon_{mf}) (1 - \delta) = 31541 \text{ g}$$

t) Diameter of the bubbles halfway up the reactor:

$$\frac{d_{bm} - d_b}{d_{bm} - d_{b0}} = e^{-0.3 \cdot h / D}$$

$$d_{b0.5} = 12.9 \text{ cm}$$

u) No solution will be given

CDP12-S No solution will be given**CDP12-T** No solution will be given**CDP12-U**

(a)

Mole Balance: $\frac{dF_A}{dW} = r'_A \Rightarrow F_{A0} \frac{dX}{dW} = -r'_A$

Rate Law: $-r'_A = k_{vg} C_A$

$$k_{vg} = \frac{1/H}{R_T}$$

Stoichiometry: $C_A = C_{A0} \left(\frac{1-X}{1+\varepsilon X} \right) \frac{P}{P_0}$

$$\varepsilon = y_{A0} \delta = (0.80)(0 - 0 - 1) = -0.8$$

$$C_A = C_{A0} \left(\frac{1-X}{1-0.8X} \right) \frac{P}{P_0}$$

12-58

CDP12-U (cont'd)

$$\text{Pressure Drop: } \frac{d(P/P_o)}{dW} = \frac{-\alpha}{P_o A_c (1 - \epsilon_b) \rho_p}$$

Evaluate Parameters:

Solubility -

$$H' = 0.0068 \text{ mol/dm}^3$$

$$H = \frac{1}{RTH'} = \frac{1}{(0.0082 \frac{\text{dm}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}})(373 \text{ K})(0.0068 \frac{\text{mol}}{\text{dm}^3 \cdot \text{atm}})} = 48.08$$

Internal Diffusion and Reaction -

$$R_r = \frac{1}{\eta k}$$

$$\phi = R \sqrt{\frac{k \rho_c}{D_e}}$$

$$D_e = D_L \frac{\sigma \epsilon_p}{\tau} = (8 \times 10^{-9} \text{ m}^2/\text{s}) \frac{(0.8)(0.5)}{(3.8)} = 8.42 \times 10^{-10} \text{ m}^2/\text{s}$$

$$\phi = 0.0015875 \text{ m} \sqrt{\frac{(2 \times 10^{-5} \text{ m}^3/\text{kg} \cdot \text{s})(1500 \text{ kg/m}^3)}{(8.42 \times 10^{-10} \text{ m}^2/\text{s})}} = 9.476 \text{ m}^2/\text{s}$$

$$\eta = \frac{3}{\phi} = \frac{3}{9.476} = 0.317$$

$$R_r = \frac{1}{(0.317)(2 \times 10^{-5} \text{ m}^3/\text{kg} \cdot \text{s})} = 1.2 \times 10^5 \frac{\text{kg} \cdot \text{s}}{\text{m}^3}$$

Gas Absorption -

$$R_s = \frac{(1 - \epsilon_b) \rho_c}{H k_s a_i}$$

$$k_s a_i = 2 + 0.91 E_s^{2/3} \Rightarrow E_s = \frac{\Delta P}{\Delta L} U_s$$

$$U_s = \left(\frac{0.25 \text{ kg}}{\text{m}^2 \cdot \text{s}} \right) \left(\frac{8.206 \times 10^{-5} \text{ m}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) \left(\frac{373 \text{ K}}{50 \text{ atm}} \right) \left(\frac{1 \text{ mol}}{0.0072 \text{ kg}} \right) = 0.0212 \text{ m/s}$$

$$E_s = (30 \text{ kPa/m})(0.0212 \text{ m/s}) = 0.638 \text{ kPa/s} = 13.32 \frac{\text{ft} \cdot \text{lb}_f}{\text{ft}^3 \cdot \text{s}}$$

$$k_s a_i = 2 + 0.91(13.32)^{2/3} = 7.11 \text{ s}^{-1}$$

$$R_s = \frac{(1 - 0.35)(1500 \text{ kg/m}^3)}{(48.08)(7.11 \text{ s}^{-1})} = 2.85 \frac{\text{kg} \cdot \text{s}}{\text{m}^3}$$

12-59

CDP12-U (cont'd)

Transport from gas - liquid interface to bulk liquids -

$$R_i = \frac{(1 - \epsilon_b) \rho_p}{k_i a_i}$$

$$Re_L = \frac{G d_p}{\mu_L} = \frac{(8 \text{ kg/m}^2 \cdot \text{s})(0.003175 \text{ m})}{0.003 \text{ kg/m} \cdot \text{s}} = 8.467$$

$$Ga = \frac{d_p^3 \rho_L^2 g}{\mu_L^2} = \frac{(0.003175 \text{ m})^3 (900 \text{ kg/m}^3)^2 (9.8 \text{ m/s}^2)}{(0.003 \text{ kg/m} \cdot \text{s})^2} = 28,096$$

$$Sc = \frac{\mu_L}{\rho_L D_L} = \frac{(0.003 \text{ kg/m} \cdot \text{s})}{(900 \text{ kg/m}^3)(8 \times 10^{-9} \text{ m}^2/\text{s})} = 416.67$$

From the correlation for organic liquids,

$$k_i a_i = D_L \left(16.8 \frac{Re_L^{1/4} Sc^{1/2}}{Ga^{0.22}} \right) = 8 \times 10^{-5} \text{ cm}^2/\text{s} \left[\frac{(16.8)(8.467)^{1/4} (416.67)^{1/2}}{(28,096)^{0.22}} \right] = 4.915 \times 10^{-3} \text{ s}^{-1}$$

$$R_i = \frac{(1 - 0.35)(1500 \text{ kg/m}^3)}{4.915 \times 10^{-3} \text{ s}^{-1}} = 2.32 \times 10^5 \frac{\text{kg} \cdot \text{s}}{\text{m}^3}$$

Resistance from bulk liquid to catalyst -

$$R_c = \frac{1}{k_c a_p}$$

$$a_p = \frac{6}{\rho_p d_p} = \frac{6}{(1500 \text{ kg/m}^3)(0.003175 \text{ m})} = 1.26 \text{ m}^2/\text{kg}$$

$$Sh = 0.266 Re^{1.15} Sc^{1/3} = (0.266)(8.467)^{1.15} (416.67)^{1/3} = 19.69$$

$$k_c = \frac{Sh D_L}{d_p} = \frac{(19.69)(8 \times 10^{-9} \text{ m}^2/\text{s})}{(0.003175 \text{ m})} = 4.96 \times 10^{-5} \text{ m/s}$$

$$R_c = \frac{1}{(4.96 \times 10^{-5} \text{ m/s})(1.26 \text{ m}^2/\text{kg})} = 0.16 \times 10^5 \frac{\text{kg} \cdot \text{s}}{\text{m}^3}$$

Total Resistance :

$$R_T = R_c + R_i + R_b + R_R = 0.16 \times 10^5 + 2.32 \times 10^5 + 2.85 + 1.2 \times 10^5 = 3.68 \times 10^5 \frac{\text{kg} \cdot \text{s}}{\text{m}^3}$$

Use these equations in POLYMATH to generate the following program and desired graph:

12-60

CDP12-U (cont'd)

CDP12-U Trickle Bed Reactor

Equations:

$$d(x)/d(w) = -r_a / f_{ao}$$

$$d(P)/d(w) = -a/P_o/A_c / (1 - e_b) / \rho$$

$$H = 48.08$$

$$R_t = 3.6825$$

$$c_{ao} = 70$$

$$a = 0.296$$

$$P_o = 50$$

$$A_c = 0.785$$

$$e_b = 0.35$$

$$\rho = 1500$$

$$f_{ao} = 8 \cdot A_c$$

$$c_a = c_{ao} \cdot (1 - x) / (1 - 0.5 \cdot x) \cdot P$$

$$k_{vg} = 1/H/R_t$$

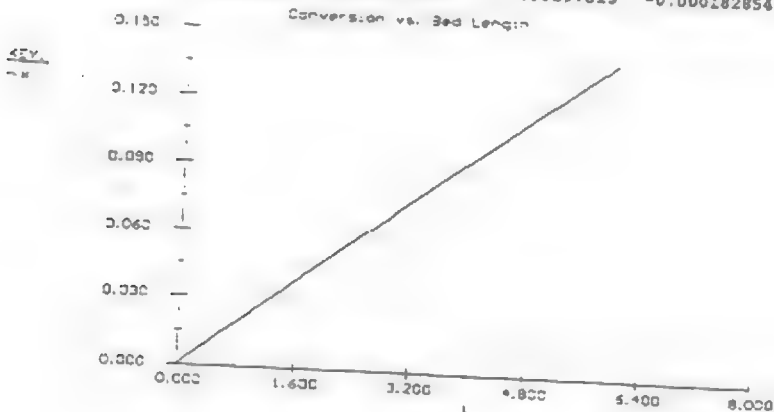
$$L = w / (1 - e_b) / \rho / A_c$$

$$r_a = -k_{vg} \cdot c_a$$

$$w_o = 0, \quad w_f = 4600$$

CDP12-U Trickle Bed Reactor

Variable	Initial value	Maximum value	Minimum value	Final value
w	0	4600	0	4600
x	0	0.139475	0	0.139475
P	50	50	49.9644	49.9644
H	48.08	48.08	48.08	48.08
Rt	368000	368000	368000	368000
c _{ao}	70	70	70	70
a	0.296	0.296	0.296	0.296
P _o	50	50	50	50
A _c	0.785	0.785	0.785	0.785
e _b	0.35	0.35	0.35	0.35
ρ	1500	1500	1500	1500
f _{ao}	6.28	6.28	6.28	6.28
c _a	3500	3500	3235.32	3235.32
k _{vg}	5.65181e-08	5.65181e-08	5.65181e-08	5.65181e-08
L	0	6.01013	0	6.01013
r _a	-0.000197813	-0.000182854	-0.000197813	-0.000182854



12-61

(b)

Percentages :

$$\text{Gas Absorption} = \frac{2.85}{3.68 \times 10^5} = 7.74 \times 10^{-6} = 7.74 \times 10^{-6} = 7.74 \times 10^{-4}\%$$

$$\text{Bulk liquid to catalyst} = \frac{0.16}{3.68} = 0.0435 = 4.35\%$$

$$\text{Internal diffusion and reaction} = \frac{1.2}{3.68} = 0.3261 = 32.61\%$$

$$\text{Gas interface to bulk liquid} = \frac{2.32}{3.68} = 0.6304 = 63.04\%$$

- (c) Changing the gas flow rate effects only the resistance due to gas absorption. Since the percent resistance of this step is so small, the total resistance is essentially the same and the conversion will be virtually unaffected.
- (d) Decreasing the flow of liquid, increasing the initial pressure, and increasing the initial concentration of aromatics in the feed all cause an increase in conversion.

Problem P13-1

No solution will be given.

P13-2A

Part (a) No solution will be given.

Part (b) See p 905

Part (c)

The conversions of the asymmetric distributions in both models are greater than the corresponding conversions in the bimodal distributions

The average primary reactant exit concentrations C_{Abar} and C_{Bbar} are greater in both models for the asymmetric distribution results over the bimodal whereas the average product exit concentrations C_{Cbar} , C_{Dbar} and C_{Ebar} are lower.

The selectivities of both models are greater in the asymmetric distribution results over the bimodal ones with the exception of S_{CD} in the maximum mixedness model.

Comparison of the asymmetric distribution results with the bimodal distribution results for both the segregation and maximum mixedness models yield similar outcomes except the values are slightly different.

Hence the generalisation may be made that if one model is used (segregation or maximum mixedness) and results are obtained for the different RTD's (asymmetric and bimodal in this Example) then these results will be similar for the other model. Comparison between results from different RTD's is model independent.

Part (d)

Liquid phase, third order, maximum mixedness model

Rate law :

$$-r_A = k \cdot C_A^3$$

$$C_A = C_{AO} \cdot (1 - x)$$

$$r_A = -k \cdot C_{AO}^3 \cdot (1 - x)^3$$

$$\frac{r_A}{C_{AO}} = -k \cdot C_{AO}^2 \cdot (1 - x)^3$$

$$\text{where } k \cdot C_{AO}^2 = 0.08 / \text{min}$$

P13-2 cont'd

13-2d

Equations:

Initial value

$$d(x)/d(z) = -(-.08 \cdot (1-x)^3) - (E/(1-F) \cdot x)$$

0

$$\text{lam} = 200 - z$$

$$E1 = 4.44658e-10 \cdot \text{lam}^4 - 1.1802e-7 \cdot \text{lam}^3 + 1.35358e-5 \cdot \text{lam}^2 - 0.0865652 \cdot \text{lam} + 0.028004$$

$$E2 = -2.64e-9 \cdot \text{lam}^3 + 1.3618e-6 \cdot \text{lam}^2 - 0.00024069 \cdot \text{lam} + 0.015011$$

$$F1 = 4.44658e-10/5 \cdot \text{lam}^5 - 1.1802e-7/4 \cdot \text{lam}^4 + 1.35358e-5/3 \cdot \text{lam}^3 - 0.000865652/2 \cdot \text{lam}^2 + 0.028004 \cdot \text{lam}$$

$$F2 = -(-9.30769e-8 \cdot \text{lam}^3 + 5.02846e-5 \cdot \text{lam}^2 - 0.00941 \cdot \text{lam} + 0.61823)$$

$$1-1)$$

$$E = \text{if}(\text{lam} \leq 70) \text{ then } (E1) \text{ else } (E2)$$

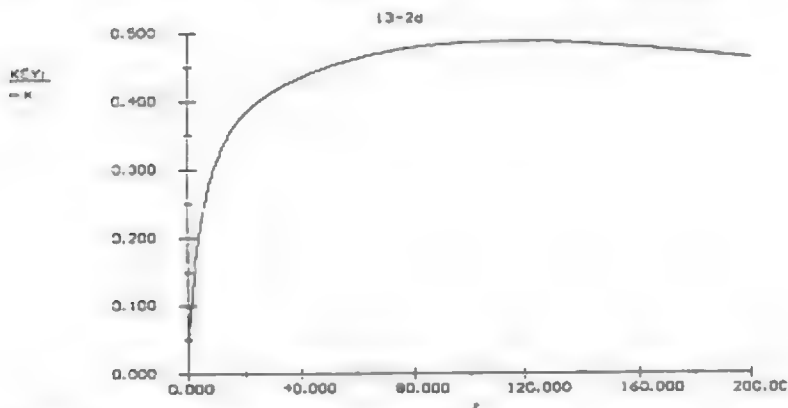
$$F = \text{if}(\text{lam} \leq 70) \text{ then } (F1) \text{ else } (F2)$$

$$EF = E/(1-F)$$

$$z_0 = 0, \quad z_f = 200$$

13-2d

Variable	Initial value	Maximum value	Minimum value	Final value
z	0	200	0	200
x	0	0.48673	0	0.461431
lam	200	200	0	0
E1	0.163598	0.163598	0.00287273	0.028004
E2	0.000225	0.015011	0.000225	0.015011
F1	5.63334	5.63334	0	0
F2	0.997	0.997	0.381769	0.381769
E	0.000225	0.028004	0.000225	0.028004
F	0.997	0.997	0	0
EF	0.075005	0.075005	0.0220679	0.028004



At $z = 200$, i.e. $\lambda = 0$ (exit), conversion $x = 46.1\%$

The increase in reaction order from 2nd to 3rd has the effect of decreasing the exit conversion by 10 %. Once the concentration of A drops below 1 mol/dm³ then the rate falls rapidly, and C_A is not consumed so quickly, resulting in a smaller conversion.

P13-2 cont'd

Part (e)

Liquid phase, half order, maximum mixedness model

Rate law :

$$-r_A = k \cdot C_A^{1/2}$$

$$C_A = C_{A0} \cdot (1 - x)$$

$$r_A = -k \cdot C_{A0}^{1/2} \cdot (1 - x)^{1/2}$$

$$\frac{r_A}{C_{A0}} = -k \cdot C_{A0}^{-1/2} \cdot (1 - x)^{1/2} \quad \text{where } k \cdot C_{A0}^{-1/2} = 0.08 \text{ /min}$$

13-2d

Variable	Initial value	Maximum value	Minimum value	Final value
z	0	200	0	200
x	0	0.641149	0	0.599649
lam	200	200	0	0
E1	0.163598	0.163598	0.00287273	0.028004
E2	0.000225	0.015011	0.000225	0.015011
F1	5.63334	5.63334	0	0
F2	0.997	0.997	0.381769	0.381769
E	0.000225	0.028004	0.000225	0.028004
F	0.997	0.997	0	0
EF	0.075005	0.075005	0.022068	0.028004

At $z = 200$, i.e. $\lambda = 0$ (exit), conversion $x = 60.0 \%$

The decrease in reaction order from 2nd to 1/2 has the effect of increasing the exit conversion by 4 %. The smaller the dependency of the rate on C_A means that when C_A falls below 1 mol/dm³ then the rate of consumption of A does not fall as rapidly (as the 2nd order reaction) and hence resulting in a larger conversion.

Part (f) No solution will be given.

Part (g) No solution will be given.

Part (h)

First order, liquid phase, adiabatic, irreversible, completely segregated.

Design equation for a batch globule, constant volume :

$$\frac{dX}{dt} = k \cdot (1 - X)$$

P13-2 cont'd

$$\text{where } k(T) = k_0 \exp\left[\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] = 0.1 \exp\left[\frac{30000}{8.314}\left(\frac{1}{320} - \frac{1}{T}\right)\right]$$

$$\text{and } T(K) = T_0 + \left(\frac{-\Delta H_{rx}}{C_{pA}}\right) \cdot X = 320 + 150X$$

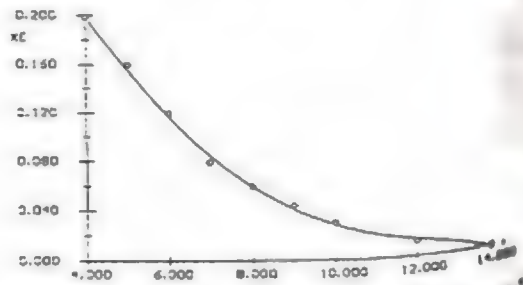
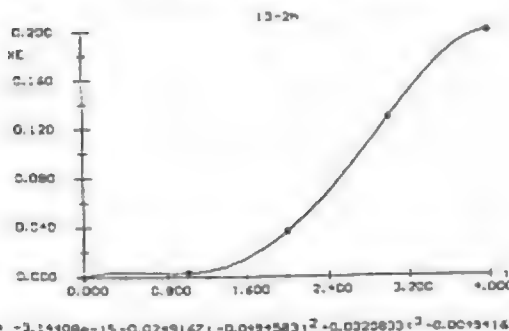
Use POLYMATH for $X(t, T)$ for $t = 1$ to 14 mins.

t (min)	E(t) (/min)	X(t, T)	E(t).X(t, T) (/min)
0	0.000	0.000	0.000
1	0.020	0.132	0.003
2	0.100	0.359	0.036
3	0.160	0.799	0.128
4	0.200	0.998	0.199
5	0.160	1.000	0.160
6	0.120	1.000	0.120
7	0.080	1.000	0.080
8	0.060	1.000	0.060
9	0.044	1.000	0.044
10	0.030	1.000	0.030
12	0.012	1.000	0.012
14	0.000	1.000	0.000

$E(t)$ for $t = 1$ to 14 min obtained from Example 13-1, gives $X(t, T) \cdot E(t)$ (min^{-1}) and evaluating the integral :

$$\bar{X} = \int_0^t X(t, T) \cdot E(t) dt \quad \text{gives the mean conversion}$$

The equation of the curve $X(t, T) \cdot E(t)$ may be found by individual polynomial fitting for the rising and falling limbs of the curve and hence the integral can be evaluated reasonably accurately.



$$P(t) = -2.14109e-15 + 0.0249167t - 0.0034583t^2 + 0.0322833t^3 - 0.00434167t^4$$

13-4

P13-2 cont'd

13-2b

Equations:

$$d(x)/d(t) = k^*(1-x)$$

$$d(xbar)/d(t) = \text{if}(t \leq 4) \text{ then}(E1) \text{ else}(E2)$$

$$E1 = 0.0241679 * t - 0.0494583 * t^2 + 0.0320833 * t^3 - 0.00454167 * t^4$$

$$E2 = 0.389124 - 0.0401033 * t - 0.00415685 * t^2 + 0.000696906 * t^3 - 2.4096$$

$$4e-5 * t^4$$

$$T = 320 + (150 * x)$$

$$k = 0.1 * \exp((30000/8.314) * ((1/320) - (1/T)))$$

$$t_0 = 0, \quad t_f = 14$$

Initial value

0

0

13-2b

<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
t	0	14	0	14
x	0	1	0	1
xbar	0	0.891414	0	0.891414
E1	0	0.196086	-95.7917	-95.7917
E2	0.389124	0.389124	-0.000442038	-0.000442038
T	320	470	320	470
k	0.1	3.65534	0.1	3.65534

The mean conversion Xbar, the integral, is estimated to be 89 %.

The reaction is adiabatic and exothermic as the temperature increases to a maximum of 470 K once the batch conversions within the globules has reached 100% which occurs after only ~ 3 minutes. Hence, the adiabatic increase in temperature considerably increases the rate at which conversion increases with time and hence also the final value. It is noted that the isothermal batch and mean conversion only reach 75% and 38% respectively after 14 minutes, much less than the respective conversions in the adiabatic exothermic case.

Part (i) No solution will be given.

Part (j) No solution will be given for Example 13-8

See Part (h) except :

$$T(K) = T_0 + \left(\frac{-\Delta H_{rx}}{C_{pA}} \right) \cdot X = 320 - 100X$$

P13-2 cont'd

13-2h

<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
t	0	14	0	14
x	0	0.41027	0	0.41027
xbar	0	0.245657	-0.000736912	0.245657
E1	0	2.12301	-0.00140392	2.12301
E2	0.0257813	0.0482985	-0.000115754	-0.000115754
T	320	320	278.973	278.973
k	0.1	0.1	0.0190458	0.0190458

The mean conversion \bar{X} , the integral, is estimated to be 25 %.

The reaction is adiabatic and endothermic as the temperature decreases to a minimum of 279 K after 14 minutes by which time the batch conversions within the globules have reached 41 %. Hence the decrease in temperature considerably decreases the rate at which conversion increases with time and hence also the final value. It is noted that the isothermal batch and mean conversion reach 75 % and 38 % respectively after 14 minutes, much more than the respective conversions in the adiabatic endothermic case.

Part (k)

See Example 8-12 for solution and Table E8-12.1 for POLYMATH equations.

Let $t_m = 1.26$ s

P13-2(k)

Equations:

$d(T)/d(t) = 2$

$C_p = 200$

$cao = .3$

$To = 283$

$\tau_{au} = 0.021$

$Dh1 = -55000$

$Dh2 = -71500$

$vo = 1000$

$E2 = 27000$

$E1 = 9900$

$UA = 40000$

$Ta = 330$

$k2 = 4.58 \cdot \exp\{(E2/1.987) \cdot ((1/500) - (1/T))\}$

$k1 = 3.3 \cdot \exp\{(E1/1.987) \cdot ((1/300) - (1/T))\}$

$ca = cao / (1 + (\tau_{au} \cdot k1))$

$kappa = UA / (vo \cdot cao) / C_p$

$G = \tau_{au} \cdot k1 / (1 + k1 \cdot \tau_{au}) \cdot Dh1 - k1 \cdot \tau_{au} \cdot k2 \cdot \tau_{au} \cdot Dh2 / ((1 + \tau_{au} \cdot k1) \cdot (1 + \tau_{au} \cdot k2))$

$Tc = (To + kappa \cdot Ta) / (1 + kappa)$

$Cb = \tau_{au} \cdot k1 \cdot ca / (1 + k2 \cdot \tau_{au})$

$R = C_p \cdot (1 + kappa) \cdot (T - Tc)$

$Cc = cao - ca - Cb$

$F = G - R$

$t_0 = 0, \quad t_f = 500$

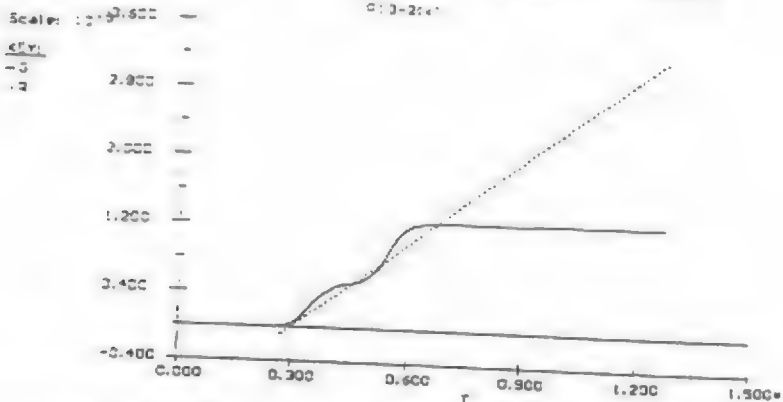
Initial value

273

P13-2 cont'd

P13-2(k)

Variable	Initial value	Maximum value	Minimum value	Final value
τ	0	500	0	500
T	273	1273	273	1273
C_p	200	200	200	200
c_{ao}	0.3	0.3	0.3	0.3
T_o	283	283	283	283
τ_{au}	0.021	0.021	0.021	0.021
Dh1	-55000	-55000	-55000	-55000
Dh2	-71500	-71500	-71500	-71500
v_o	1000	1000	1000	1000
E_2	27000	27000	27000	27000
E1	9900	9900	9900	9900
UA	40000	40000	40000	40000
T_a	330	330	330	330
k_2	$7.02951e-10$	$6.72612e+07$	$7.02951e-10$	$6.72612e+07$
k_1	0.638507	$1.07516e+06$	0.638507	$1.07516e+06$
ca	0.296031	0.296031	$1.32865e-05$	$1.32865e-05$
kappa	0.666667	0.666667	0.666667	0.666667
G	727.718	126494	727.718	126494
T_c	301.8	301.8	301.8	301.8
C_b	0.00396937	0.284642	$2.12382e-07$	$2.12382e-07$
R	-9600	323733	-9600	323733
C_c	$5.86111e-14$	0.299987	$5.86111e-14$	0.299987
F	10127.7	19689.2	-197239	-197239



With a $t_m = 1.26$ s (0.021 min) rather than 0.01 min it is clear that only three steady states exist rather than five.

SS	T	C_A	C_B	C_C
1	462	0.012	0.285	0.003
2	530	0.003	0.207	0.09
3	677	0.0004	0.0025	0.2974

Problem P13-3c

Maximum mixedness model :
$$\frac{dC_A}{d\lambda} = k \cdot C_A + \frac{E(\lambda)}{1-F(\lambda)} (C_A - C_{A0})$$

rearranging :
$$\frac{dC_A}{d\lambda} - \left[k + \frac{E(\lambda)}{1-F(\lambda)} \right] C_A = -\frac{C_{A0} \cdot E(\lambda)}{1-F(\lambda)}$$

Using the integrating factor :
$$\frac{d \left[\frac{C_A}{C_{A0}} e^{-\int \left[k + \frac{E(\lambda)}{1-F(\lambda)} \right] d\lambda} \right]}{d\lambda} = -\frac{E(\lambda)}{1-F(\lambda)} e^{-\int \left[k + \frac{E(\lambda)}{1-F(\lambda)} \right] d\lambda}$$

$$\frac{C_A}{C_{A0}} e^{-\int \left[k + \frac{E(\lambda)}{1-F(\lambda)} \right] d\lambda} = - \int \left[\frac{E(\lambda)}{1-F(\lambda)} e^{-\int \left[k + \frac{E(\lambda)}{1-F(\lambda)} \right] d\lambda} \right] d\lambda$$

$$\frac{C_A}{C_{A0}} e^{-\lambda \cdot k} e^{-\int \left[\frac{E(\lambda)}{1-F(\lambda)} \right] d\lambda} = - \int \left[\frac{E(\lambda)}{1-F(\lambda)} e^{-k \cdot \lambda} e^{-\int \left[\frac{E(\lambda)}{1-F(\lambda)} \right] d\lambda} \right] d\lambda$$

But $E(\lambda) d(\lambda) = dF(\lambda)$

gives :
$$e^{-\int \left[\frac{E(\lambda)}{1-F(\lambda)} \right] d\lambda} = e^{-\int \frac{dF}{1-F(\lambda)}} = e^{d[\ln(1-F(\lambda))]} = (1-F(\lambda))$$

changing the variable from λ to t in the RHS integral :

$$\frac{C_A}{C_{A0}} e^{-k\lambda} (1-F(\lambda)) = \int_{\lambda}^{\infty} \left[\frac{E(t)}{1-F(t)} e^{-k\lambda} (1-F(t)) \right] dt$$

$$C_A = \frac{C_{A0} \cdot e^{k\lambda}}{1-F(\lambda)} \int_{\lambda}^{\infty} E(t) e^{-k\lambda} dt \quad (1)$$

Exit concentration is when $\lambda = 0$, $F(0) = 0$ hence eqn (1) becomes :

$$C_A = C_{A0} \int_0^{\infty} E(t) e^{-k\lambda} dt$$

which is the same expression as for the exit concentration for the segregation model.

Problem P13-4c

Part (a)

CSTR

$$\begin{aligned}v.(C_{A0} - C_A) &= k.C_A^n V \\&= k.C_{A0}^n (1 - X)^n V \\&= k.C_{A0}.C_{A0}^{n-1} (1 - X)^n V \\X &= k.C_{A0}^{n-1} (1 - X)^n \frac{V}{v} \\ \frac{X}{(1 - X)^n} &= k.\tau.C_{A0}^{n-1} \quad \text{for CSTR}\end{aligned}$$

PFR

$$\begin{aligned}v.C_{A0} \frac{dX}{dV} &= k.C_A^n \\ \frac{dX}{dV} &= \frac{k.C_{A0}^n}{v.C_{A0}} (1 - X)^n \\ \int_0^X \frac{dX}{(1 - X)^n} &= \frac{k.C_{A0}^{n-1}}{v} \int_0^V dV = k.\tau.C_{A0}^{n-1}\end{aligned}$$

Now evaluating

$$\begin{aligned}\int_0^X \frac{dX}{(1 - X)^n} & \quad \text{put } y = 1 - X \quad \text{limits } X = 0, y = 1 \\ & \quad dy = -dX \quad X = X, y = y\end{aligned}$$

$$-\int_1^y \frac{1}{y^n} dy = -\left[\frac{y^{1-n}}{1-n} \right]_1^y = \left[\frac{(1-X)^{1-n}}{1-n} \right]_X^1 = \frac{1}{1-n} [1 - (1-X)^{1-n}]$$

$$\frac{1}{1-n} [1 - (1-X)^{1-n}] = k.\tau.C_{A0}^{n-1} \quad \text{for PFR}$$

Equating

$$\frac{X_{CSTR}}{(1 - X_{CSTR})^n} = \frac{1}{1-n} [1 - (1 - X_{PFR})^{1-n}]$$

For $n < 1$ the conversion is greater for CSTR.

Part (b)

See CD-ROM for full length answer.

For an n th order reaction

$$-r_A = k_n C_A^n$$

$$\left. \frac{\delta^2(-r_A)}{\delta C_A^2} \right|_{C_A=C_{A^*}} = n(n-1)k_n C_{A^*}^{n-2}$$

The maximum mixedness model will give greater conversion as compared to the segregation model if

$$n(n-1) < 0$$

$$\Rightarrow n \in (0, 1)$$

Similarly, the segregation model will give greater conversion as compared to the maximum mixedness model if

$$n(n-1) > 0$$

$$\Rightarrow \text{either } n < 0 \text{ or } n > 1$$

Both models will give the same conversion if

$$n(n-1) = 0$$

$$\Rightarrow \text{either } n = 0 \text{ or } n = 1$$

Problem P13-5B (old manual solution)

The tracer experiment for the poor operation indicate that initially there is channelling in the bed, corresponding to the rapid peak in concentration. After the peak the concentration falls as the tracer flow is hindered by compacted packing in the other parts of the bed.

Part (a), (b)

The mean conversion for RTD analysis is

$$\bar{X} = \int_0^\infty (1 - e^{-kt}) \cdot E(t) \cdot dt$$

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)}$$

P13-5 cont'd

Using $E(t)$ data from the flow conditions we get the following mean conversion after evaluating the above integral.

X_A values for different operations

Flow condition	$k_1 = 0.1 \text{ hr}^{-1}$	$k_2 = 2 \text{ hr}^{-1}$
Poor operation	0.1	0.364
Good operation	0.4	0.518

Part (c)

Results point to the importance of flow condition in achieving high conversion.

Problem P13-6a

Irreversible liquid phase, half order, segregation model.

$$\text{Mean conversion} \quad \bar{X} = \int_0^{\infty} X(t) \cdot E(t) dt = 0.1$$

Assume a normal distribution for $E(t)$:

$$E(t) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(t-\tau)^2}{2\sigma^2}\right] = \frac{1}{3\sqrt{2\pi}} \exp\left[-\frac{(t-5)^2}{2 \times 3^2}\right]$$

$$\frac{dX}{dt} = k \frac{C_{A0}^{1/2}}{C_{A0}} (1-X)^{1/2} \quad \text{and } C_{A0} = 1 \text{ mol/dm}^3$$

By integrating for X at values of k_1 and inserting into the integral for mean conversion, along with the $E(t)$ function will yield $\bar{X} = 0.1$ for some value of k_1 . This is a trial and error method to estimate k_1 .

Using POLYMATH : $k_1 = 0.0205 \text{ mol}^{1/2}/\text{dm}^{1/6} \cdot \text{s}$

P13-6 cont'd

Equations:

$$d(x)/d(\tau) = k \cdot \{(1-x)^{1/2}\}$$

$$d(\bar{x})/d(\tau) = x \cdot E$$

$$k = 0.0205$$

$$\sigma = 3$$

$$\tau = 5$$

$$E = (1/(\sigma \cdot \{(23.14)^{1/2}\})) \cdot \exp(-\{(\tau - \tau)^2\}/(2 \cdot (\sigma^2)))$$

$$\tau_0 = 0, \quad \tau_f = 120$$

Initial value

0

0

<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
t	0	97.5607	0	97.5607
x	0	1	0	1
xbar	0	0.0521924	0	0.0521924
k	0.0205	0.0205	0.0205	0.0205
sigma	3	3	3	3
tau	5	5	5	5
E	0.0172787	0.0691952	1.34602e-208	1.34602e-208

Problem P13-7_R (old manual solution)

Cumulative exit age distribution function : $F(t) = \int_0^t E(t) \cdot dt$

For a negative step $F(t) = \int_0^t -\frac{d}{dt} \left[\frac{C(t)}{C_0} \right] dt = 1 - \frac{C(t)}{C_0}$

$$I(t) = \frac{v}{V} (1 - F(t)) = \frac{v}{V} \frac{C(t)}{C_0}$$

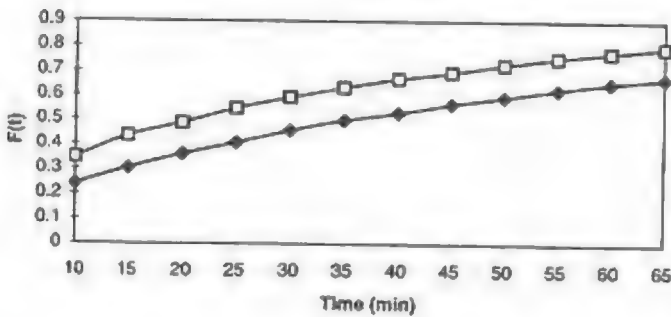
$$v = 1.15 \text{ gal/min} = 4.35 \text{ l/min}$$

$$V = \frac{\pi}{4} D^2 L = \frac{\pi}{4} (30)^2 (30) \text{ in}^3 = 347.35 \text{ litres}$$

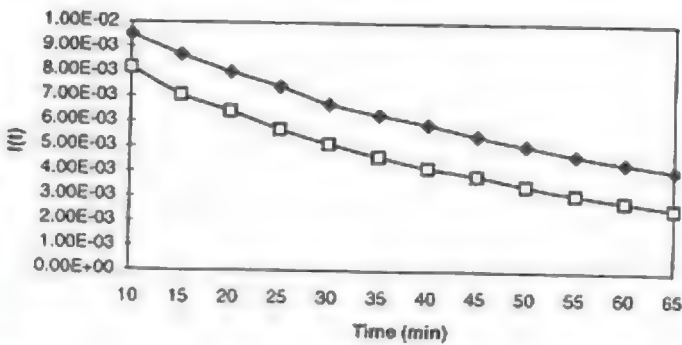
P13-7 cont'd

Time (min)	Cumulative exit age distribution $F(t)$		Internal age $I(t)$	
	170 rpm	100 rpm	170 rpm	100 rpm
10	0.239	0.347	9.51E-03	8.16E-03
15	0.305	0.434	8.69E-03	7.07E-03
20	0.361	0.487	7.99E-03	6.41E-03
25	0.408	0.546	7.40E-03	5.67E-03
30	0.457	0.591	6.70E-03	5.11E-03
35	0.498	0.631	6.28E-03	4.60E-03
40	0.528	0.667	5.90E-03	4.16E-03
45	0.564	0.693	5.45E-03	3.84E-03
50	0.593	0.724	5.08E-03	3.45E-03
55	0.624	0.752	4.70E-03	3.10E-03
60	0.65	0.774	4.38E-03	2.83E-03
65	0.671	0.795	4.11E-03	2.56E-03

Cumulative exit age distribution



Internal age distribution



P13-7 cont'd

The tracer fraction leaving the tank which has been in the tank for time t is always greater in the 100 rpm tank than the 170 rpm tank. Consequently the tracer fraction inside the tank which has been inside the tank for time t is always greater for the 170 rpm tank. This suggests that the tank operated at 100 rpm has dead zones and the tracer bypasses.

Part (b) *second order, completely segregated model*

Batch reactor eqn for a second order reaction

$$\frac{dC_A}{dt} = r_A \qquad \frac{dX}{dt} = -\frac{r_A}{C_{A0}}$$

$$\frac{r_A}{C_{A0}} = -kC_{A0}(1-X)^2$$

$$\int_0^X \frac{dX}{(1-X)^2} = \int_0^t k \cdot C_{A0} \cdot dt \qquad \frac{X}{1-X} = k \cdot C_{A0} \cdot t$$

$$X = \frac{k \cdot C_{A0} \cdot t}{1 + k \cdot C_{A0} \cdot t}$$

where $k \cdot C_{A0} = 0.05 / \text{min}$

mean conversion $\bar{X} = \int_0^1 X(t, T) \cdot E(t) dt$

	170 rpm	100 rpm
mean conversion	0.63	0.58

Part (c) *second order, maximum mixedness model*

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{A0}} + \frac{E(\lambda)}{1-F(\lambda)} \cdot X$$

Rate law :

$$-r_A = k \cdot C_A^2$$

$$C_A = C_{A0} \cdot (1-x)$$

$$r_A = -k \cdot C_{A0}^2 \cdot (1-x)^2$$

13-14

P13-7 cont'd

$$\frac{r_A}{C_{AO}} = -k \cdot C_{AO} \cdot (1-x)^2$$

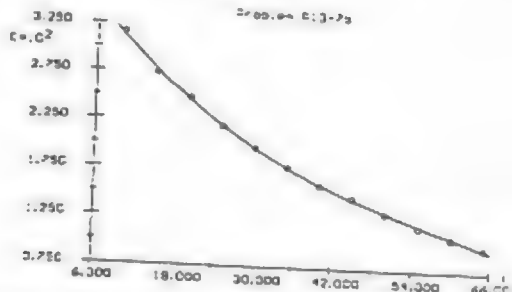
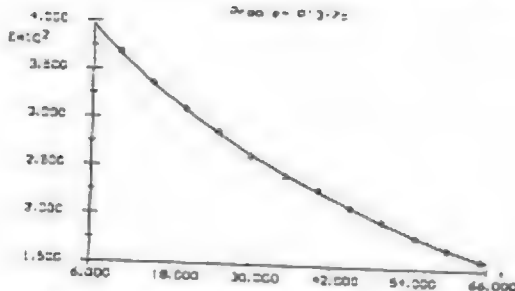
$$\text{where } k \cdot C_{AO} = 0.05 / \text{min}$$

$$E(\lambda) = \frac{C(\lambda)}{\int_0^1 C(\lambda) d\lambda}$$

$$\frac{dF}{d\lambda} = E(\lambda)$$

$$\lambda = 65 - t$$

$E(\lambda)$ is found using POLYMATH polynomial fitting



$$100 \text{ rpm} : E(\lambda) = 0.04045 - 0.001028\lambda + 1.366e-5\lambda^2 - 7.833e-8\lambda^3$$

$$170 \text{ rpm} : E(\lambda) = 0.0449 - 0.000931\lambda + 1.475e-5\lambda^2 - 1.659e-7\lambda^3 + 8.28e-10\lambda^4$$

	170 rpm	100 rpm
conversion	0.47	0.45

Problem P13-7c

Equations:

$$d(X)/d(t) = (kC_{AO} \cdot (1-X)^2) - ((K \cdot X) / (1-F))$$

$$d(F)/d(t) = -X$$

$$kC_{AO} = 0.05$$

$$\lambda = 65 - t$$

$$Z = 0.0449 - (0.000931 \cdot \lambda) + ((1.475e-5) \cdot (\lambda^2)) - ((1.659e-7) \cdot (\lambda^3)) + ((8.28e-10) \cdot (\lambda^4))$$

$$t_0 = 0, \quad t_f = 65$$

Initial value

$$0$$

$$0.999$$

Problem P13-7c

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	65	0	65
X	0	0.474937	0	0.474937
F	0.999	0.999	-0.754792	-0.754792
kC _{AO}	0.05	0.05	0.05	0.05
λ	65	65	0	0
Z	0.0159238	0.0449	0.0159238	0.0449

P13-7 cont'd

Part (d)

As in Part (b) segregation model, second order: except adiabatic

As in Part (c) maximum mixedness model, second order: except adiabatic

$$\text{where } k(T) = k_0 \cdot \exp\left[\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] = 0.05 \exp\left[\frac{5000}{1.987}\left(\frac{1}{320} - \frac{1}{T}\right)\right]$$

$$\text{and } T(K) = T_0 + \left(\frac{-\Delta H_{rx}}{C_{pA}}\right) \cdot X = 320 + 80X$$

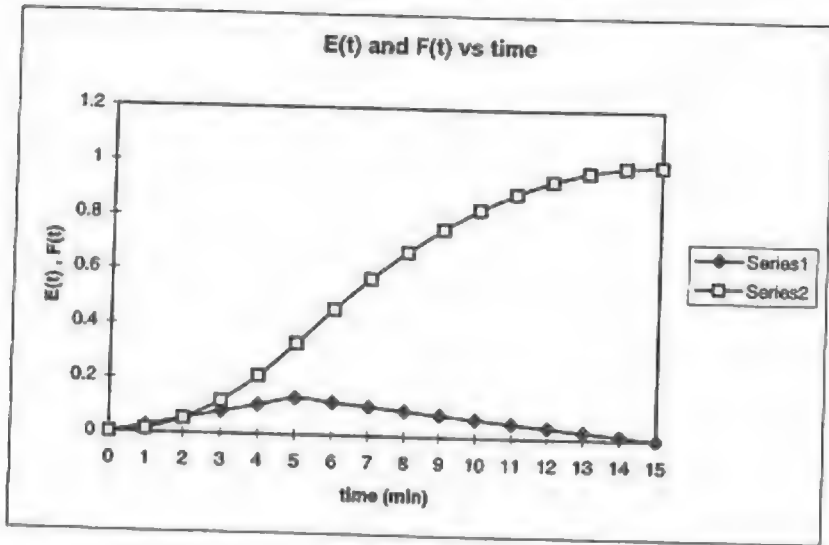
$$C_{A0} = ?$$

Problem P13-8_B

Part (a)

t (min)	C (10e-6 mol)	E(t)	F(t)	t.E(t)
0	0	0	0	0
1	0.1	0.026667	0.013333	0.026667
2	0.2	0.053333	0.053333	0.106667
3	0.3	0.08	0.12	0.24
4	0.4	0.106667	0.213333	0.426667
5	0.5	0.133333	0.333333	0.666667
6	0.45	0.12	0.46	0.72
7	0.4	0.106667	0.573333	0.746667
8	0.35	0.093333	0.673333	0.746667
9	0.3	0.08	0.76	0.72
10	0.25	0.066667	0.833333	0.666667
11	0.2	0.053333	0.893333	0.586667
12	0.15	0.04	0.94	0.48
13	0.1	0.026667	0.973333	0.346667
14	0.05	0.013333	0.993333	0.186667
15	0	0	1	0
int C = 3.75E-06 mol.s/dm3			int t.E(t) = 6.666667	
int E(t) = 0.9999975				

P13-8 cont'd



Part (b)

Mean residence time , $t_m = \int_0^{\infty} t \cdot E(t) dt = 6.67 \text{ min (see table)}$

Volume $V = t_m \cdot v = 6.667 \cdot 150 = 1000 \text{ gal.}$

Part (c)

PFR, second order

$$v \cdot C_{A0} \frac{dX}{dV} = k \cdot C_A^2$$

$$\int_0^X \frac{dX}{(1-X)^2} = \frac{k \cdot C_{A0}}{v} \int_0^V dV$$

where $V = 1000 \text{ gal}$, $v = 150 \text{ gal/min}$, $k \cdot C_{A0} = 1.2 / \text{min}$

$$\frac{X}{1-X} = 1.2 \cdot \frac{1000}{150}$$

gives $X = 0.889$ by iteration

P13-8 cont'd

Part (d)

CSTR, second order

$$v.(C_{A0} - C_A) = k.C_A^2 V$$

$$\frac{(C_{A0} - C_A)}{C_A} = \frac{V}{v} k.C_{A0}.(1 - X)^2$$

$$\frac{X}{(1 - X)^2} = \frac{V}{v} k.C_{A0}$$

where $V = 1000$ gal, $v = 150$ gal/min, $k.C_{A0} = 1.2$ /min

gives $X = 0.703$ by iteration

Part (e)

Completely segregated

Batch reactor eqn :

$$\frac{dC_A}{d\lambda} = kC_A^2$$

$$\frac{dX}{d\lambda} = -kC_{A0}(1 - X)^2$$

$$\bar{X} = \int_0^1 -X(\lambda)E(\lambda)d\lambda$$

where $E(t) = \text{if } (t \leq 5) \text{ then } (0.1333 / 5) * t \text{ else } (0.2 - (0.13333 / 10) * t)$

Problem P13-8e

Equations:

$$d(X)/d(\tau) = kC_{A0}*(1-X)^2$$

$$d(\bar{x})/d(\tau) = E*X$$

$$kC_{A0} = 1.2$$

$$E = \text{if } (\tau \leq 5) \text{ then } (0.0266667 * \tau) \text{ else } (0.2 - (0.0133333 * \tau))$$

$$\text{lam} = 15 - \tau$$

$$\tau_0 = 0, \quad \tau_f = 15$$

Problem P13-8e

Variable	Initial value	Maximum value	Minimum value	Final value
τ	0	15	0	15
X	0	0.947368	0	0.947368
\bar{x}	0	0.860399	0	0.860399
kC_{A0}	1.2	1.2	1.2	1.2
E	0	0.133322	0	5e-06
lam	15	15	0	0

P13-8 cont'd

Using POLYMATH gives mean conversion $\bar{x} = 0.86$ at $t = 15$ min

Part (f)

Maximum mixedness

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{A0}} + \frac{E(\lambda)}{1-F(\lambda)} \cdot X$$

Rate law :

$$-r_A = k \cdot C_A^2$$

$$C_A = C_{A0} \cdot (1-x)$$

$$r_A = -k \cdot C_{A0}^2 \cdot (1-x)^2$$

$$\frac{r_A}{C_{A0}} = -k \cdot C_{A0} \cdot (1-x)^2 \quad \text{where } k \cdot C_{A0} = 1.2 / \text{min}$$

$$\frac{dF}{d\lambda} = E(\lambda) \quad \lambda = 15 - t$$

where $E(\lambda) = \text{if } (\lambda \geq 5) \text{ then } (0.3999 - (0.1333 / 5) * \lambda) \text{ else } ((0.13333 / 10) * t)$

Problem P13-8f

Equations:

$$d(F)/d(t) = -E$$

$$d(X)/d(t) = (kC_{A0} * ((1-X)^2)) - (E * X / (1-F))$$

$$kC_{A0} = 1.2$$

$$\lambda = 15 - t$$

$$E = \text{if}(\lambda \geq 10) \text{ then } (0.39999 - (0.026667 * \lambda)) \text{ else } (0.013333 * \lambda)$$

$$t_0 = 0, \quad t_f = 15$$

Problem P13-8f

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	15	0	15
F	0.9999	0.9999	-1.24957e-05	-1.24957e-05
X	0	0.853917	0	0.853917
kCao	1.2	1.2	1.2	1.2
lam	15	15	0	0
E	-1.5e-05	0.133318	-1.5e-05	0

Using POLYMATH gives $X = 0.854$

13-19

P13-8 cont'd

Part (g)

$$k(T) = k_o \cdot \exp \left[\frac{E}{R} \left(\frac{1}{T_o} - \frac{1}{T} \right) \right] = k_o \cdot \exp \left[\frac{30000}{8314} \left(\frac{1}{325} - \frac{1}{T} \right) \right]$$

$$\text{and } T(K) = T_o + \left(\frac{-\Delta H_{rx}}{C_{pA}} \right) X = 320 + 150X$$

But $k(325K) = ?$ and $C_{Ao} = ?$

Part (h)

$$k(T) = k_o \cdot \exp \left[\frac{E}{R} \left(\frac{1}{T_o} - \frac{1}{T} \right) \right] = k_o \cdot \exp \left[\frac{10000}{1.987} \left(\frac{1}{325} - \frac{1}{T} \right) \right]$$

$$\text{and } T(K) = T_o + \left(\frac{-\Delta H_{rx}}{C_{pA}} \right) X = 325 - 500X$$

But $k(325K) = ?$ and $C_{Ao} =$

Problem P13-9_A

3rd order

Part (a)

PFR

Design equation

$$v_o C_{Ao} \frac{dX}{dV} = k \cdot C_A \cdot C_B^2$$

$$C_A = C_{Ao}(1 - X)$$

$$C_B = C_{Bo}(1 - X)$$

$$\int_0^X \frac{dX}{(1 - X)^3} = k \cdot C_{Bo}^2 \frac{V}{v}$$

Let

$$y = 1 - X, \quad dy = -dX$$

$$\int -\frac{dy}{y^3} = \left[\frac{1}{2y^2} \right] = \left[\frac{1}{2(1 - X)^2} \right]_0^X = k \cdot C_{Bo}^2 \cdot \frac{V}{v_o}$$

P13-9 cont'd

$$\frac{1}{(1-X)^2} - 1 = 2.k.C_{B0}^2 \cdot \frac{V}{v}$$

$$1 - 2X + X^2 = \frac{1}{1 + 2.k.C_{B0}^2 \cdot \frac{V}{v}}$$

$$\text{Using the quadratic solution } X = \frac{2 \pm \sqrt{4 - 4 \left[1 - \frac{1}{1 + 2.k.C_{B0}^2 \cdot \frac{V}{v}} \right]}}{2}$$

Substituting the values

$$X = 1 \pm \sqrt{\left[\frac{1}{1 + 2.k.C_{B0}^2 \cdot \frac{V}{v}} \right]} = 1 - 0.168 = 0.832$$

The conversion for a PFR $X = 83.2 \%$

CSTR

Design equation

$$v_0.(C_{A0} - C_A) = -r_A.V$$

$$-r_A = k.C_A.C_B^2$$

$$C_A = C_{A0}(1 - X)$$

$$C_B = C_{B0}(1 - X)$$

$$\frac{C_{A0} - C_A}{C_{A0}} = X$$

$$X = k.C_{B0}^2.(1 - X)^3 \frac{V}{v}$$

Substituting the values and iteration gives:

The conversion for a CSTR $X = 66.2 \%$

P13-9 cont'd

Laminar flow , completely segregated

$$E(t) = 0 \quad \text{for} \quad t < \tau/2$$

$$= \tau^2 / 2t^3 \quad \text{for} \quad t \geq \tau/2$$

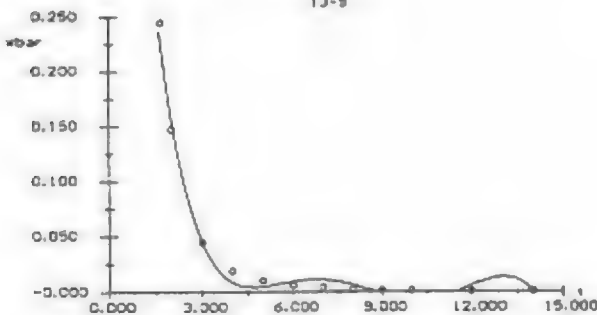
$$\tau = V / v = 1000 / 10 = 100 \text{ s} = 1.67 \text{ min}$$

$$\bar{X} = \int_0^\infty X(t) \cdot E(t) dt$$

where

$$X(t) = 1 - \sqrt{\frac{1}{1 + 2 \cdot k \cdot C_{B0}^2 \cdot t}}$$

13-9



$$P(t) = 0.910432 - 0.635652t + 0.169962t^2 - 0.021569t^3 + 0.00130028t^4$$

$$- 2.99258e-05t^5$$

$$\text{variance} = 0.00018111$$

The integral xbar gives mean conversion = 22 %

Part (b)

Segregated model

$$-\frac{dN_A}{dt} = -r_A \cdot V$$

Batch reactor

$$N_A = N_{A0}(1 - X)$$

$$N_{A0} \frac{dX}{dt} = k \cdot C_A \cdot C_B^2 \cdot V$$

$$C_A = C_{A0}(1 - X)$$

$$C_B = C_{B0}(1 - X)$$

13-22

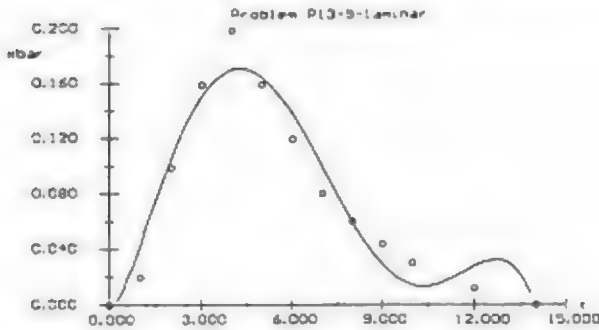
P13-9 cont'd

$$\int_0^x \frac{dX}{(1-X)^3} = k \cdot C_{B0}^2 \cdot t$$

Similarly

$$X(t) = 1 - \sqrt{\frac{1}{1 + 2 \cdot k \cdot C_{B0}^2 \cdot t}}$$

$$\bar{X} = \int_0^{\infty} X(t) \cdot E(t) dt \quad \text{and } E(t) \text{ from the given data.}$$



$$P(t) = -0.0111381 + 0.039064t + 0.020792t^2 - 0.00720741t^3 + 0.00068036t^4$$

$$-2.04051e-05t^5$$

$$\text{variance} = 0.000439956$$

Evaluation of the integral gives mean conversion for the segregation model
 $\bar{x} = 90\%$

Maximum mixedness

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{A0}} + \frac{E(\lambda)}{1 - F(\lambda)} \cdot X$$

Rate law :

$$-r_A = k \cdot C_A \cdot C_B^2$$

$$C_A = C_{A0} \cdot (1 - x)$$

$$C_B = C_{B0} \cdot (1 - x)$$

$$r_A = -k \cdot C_{A0} \cdot C_{B0}^2 \cdot (1 - x)^3 \quad \text{where } k = 10500 \text{ dm}^6 / \text{mol}^2 \cdot \text{min}$$

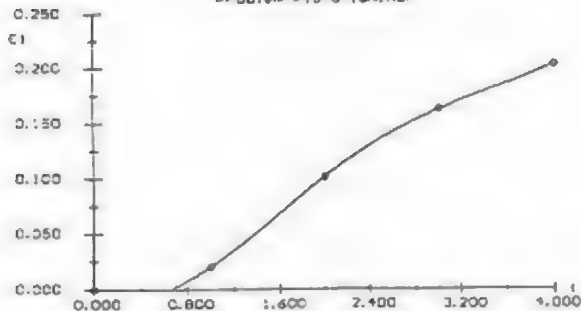
$$\frac{r_A}{C_{A0}} = -k \cdot C_{B0}^2 \cdot (1 - x)^3$$

$$\frac{dF}{d\lambda} = E(\lambda)$$

$$\lambda = 14 - t$$

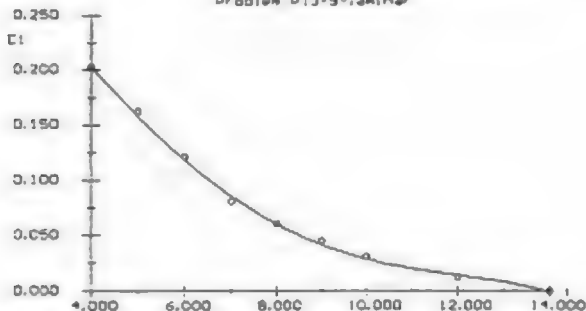
P13-9 cont'd

Problem P13-9-laminar



$$P(t) = 5.92497e-15 - 0.0575531 + 0.108335t^2 - 0.0338547t^3 + 0.00338547t^4$$

Problem P13-9-laminar



$$P(t) = 0.409357 - 0.0472643t + 0.00313845t^2 + 0.000631035t^3 - 2.25042e-05t^4$$

$$\text{variance} = 1.58574e-05$$

where $E(\lambda) =$ if $(\lambda \geq 10)$

then $(4.52e-15 - 0.05755\lambda + 0.10833\lambda^2 - 0.03385\lambda^3 + 0.003385\lambda^4)$ else
 $(0.40936 - 0.04726\lambda - 0.003138\lambda^2 + 0.000631\lambda^3 - 2.2504e-5\lambda^4)$

13-9

Equations:

$$d(F)/d(t) = -E$$

$$d(x)/d(t) = (k * cbo^2) * (1-x)^3 - (E * x / (1-F))$$

$$k = 10500$$

$$cbo = 0.313$$

$$lam = 15 - t$$

$$E1 = (4.526e-15) - (0.05755 * lam) + (0.10833 * (lam^2)) - (0.03385 * (lam^3)) + (0.003385 * (lam^4))$$

$$E2 = 0.40936 - (0.04726 * lam) - (0.003138 * (lam^2)) + (0.000631 * (lam^3)) - (2.25046e-5 * (lam^4))$$

$$E = \text{if}(lam \geq 10) \text{ then } \{E1\} \text{ else } \{E2\}$$

$$t_0 = 0, \quad t_f = 14$$

Initial value

$$0.9999$$

$$0$$

13-24

P13-9 cont'd

13-9

Variable	Initial value	Maximum value	Minimum value	Final value
c	0	14	0	14
F	0.9999	0.9999	-185.199	-185.199
x	0	0.989531	0	0.98881
k	10500	10500	10500	10500
cbo	0.313	0.313	0.313	0.313
lam	15	15	1	1
E1	80.6329	80.6329	0.020315	0.020315
E2	-0.0153204	0.35951	-0.0153204	0.35951
E	80.6329	80.6329	0.020854	0.35951

The exit conversion as estimated by the maximum mixedness model is $X = 92.7\%$

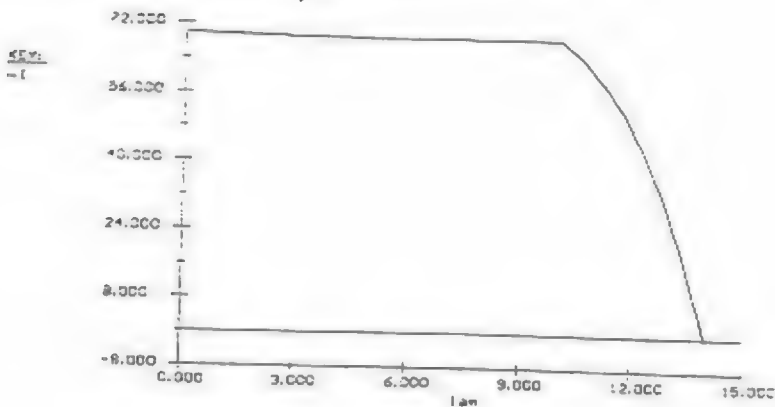
Part (c)

$$\int_0^t E(t) dt = F(t) \Rightarrow \frac{dF(t)}{dt} = E(t)$$

where $E(t)$ is obtained from the polynomial fit in Part (b).

Let $\alpha = \text{age}$

$$I(\alpha) = \frac{v}{V} [1 - F(\alpha)]$$

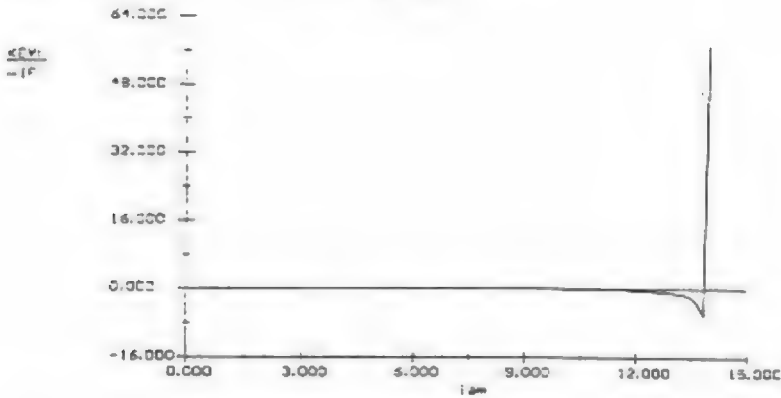


13-25

P13-9 cont'd

Intensity function

$$\Lambda\lambda = \frac{E(\lambda)}{1 - F(\lambda)}$$



Part (d)

Segregation model

$$\frac{dX}{dt} = k \cdot C_{B0}^2 (1 - X)^3$$

$$\text{where } k(T) = k_0 \cdot \exp\left[\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] = 10500 \exp\left[\frac{30000}{8.314}\left(\frac{1}{320} - \frac{1}{T}\right)\right]$$

$$\text{and } T(K) = T_0 + \left(\frac{-\Delta H_{rx}}{C_{pA}}\right) \cdot X = 320 + 150X$$

$$\bar{X} = \int_0^{\infty} X(t) \cdot E(t) dt \quad \text{and } E(t) \text{ from the given data.}$$

Evaluating $X(t, T)$ using ODE solver and then evaluating the integral \bar{x} using polyfitting gives

$$\bar{x} = 98 \%$$

Maximum mixedness model

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{A0}} + \frac{E(\lambda)}{1 - F(\lambda)} \cdot X$$

$$\frac{r_A}{C_{A0}} = -k \cdot C_{B0}^2 \cdot (1 - x)^3$$

13-26

P13-9 cont'd

where $k(T) = k_0 \cdot \exp\left[\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] = 10500 \exp\left[\frac{30000}{8.314}\left(\frac{1}{320} - \frac{1}{T}\right)\right]$

and $T(K) = T_0 + \left(\frac{-\Delta H_{rx}}{C_{pA}}\right) \cdot X = 320 + 150X$

gives $X = 99\%$

Problem P13-10_B (old manual solution)

Irreversible, first order, long tubular reactor, constant volume, isothermal.

For a PFR

$$\frac{dF_A}{dV} = -r_A$$

$$F_{A0} \frac{dX}{dV} = k \cdot C_{A0} \cdot (1 - X)$$

$$\int_0^X \frac{dX}{1 - X} = \frac{k}{u_0} \int_0^V dV$$

$$X = 1 - e^{-k\tau}$$

For $X = 0.865 \Rightarrow k\tau = 2.0$

For laminar flow with negligible diffusion, the mean conversion is given by

$$\bar{X} = \int_0^{\bar{\tau}} X(t, T) \cdot E(t) dt = \int_{\tau/2}^{\bar{\tau}} X(t) \cdot E(t) \cdot dt$$

$$X(t) \text{ used for batch} = 1 - e^{-k\tau}$$

$$E(t) \text{ for laminar flow reactor} = \frac{\tau^2}{2t^3} \quad \text{where } t \geq \frac{\tau}{2}$$

Therefore $\bar{X} = \int_{\tau/2}^{\bar{\tau}} (1 - e^{-k\tau}) \frac{\tau^2}{2t^3} dt = 1 - \int_{\tau/2}^{\bar{\tau}} \frac{e^{-k\tau} \tau^2}{2t^3} dt$

$$\bar{X} = 1 - \frac{\tau^2}{2} \int_{\tau/2}^{\bar{\tau}} \frac{e^{-k\tau} \tau^2}{t^3} dt$$

13-27

Integrate by parts :

$$u = e^{-k\tau} \quad du = -k \cdot e^{-k\tau} d\tau$$

$$dv = \frac{d\tau}{\tau^3} \quad v = -\frac{1}{2\tau^2}$$

$$\bar{X} = 1 - \frac{\tau^2}{2} \left\{ \frac{e^{-k\tau}}{2\tau^2} \right\} \Big|_{\tau/2}^{\infty} - \int_{\tau/2}^{\infty} k \cdot \frac{e^{-k\tau}}{2\tau^2} d\tau$$

$$\bar{X} = 1 - \frac{\tau^2}{2} \left\{ 0 + \frac{2e^{-k\tau/2}}{\tau^2} - \frac{k}{2} \int_{\tau/2}^{\infty} \frac{e^{-k\tau}}{\tau^2} d\tau \right\}$$

Integrate again by parts :

$$u = e^{-k\tau} \quad du = -k \cdot e^{-k\tau} d\tau$$

$$dv = \frac{d\tau}{\tau^2} \quad v = -\frac{1}{\tau}$$

$$\bar{X} = 1 - e^{-k\tau/2} + \frac{k\tau^2}{4} \left\{ \frac{e^{-k\tau}}{\tau} \right\} \Big|_{\tau/2}^{\infty} - \int_{\tau/2}^{\infty} \frac{k \cdot e^{-k\tau}}{\tau} d\tau \Big\}$$

$$\bar{X} = 1 - e^{-k\tau/2} + \frac{k\tau^2}{4} \left\{ 0 - \frac{2e^{-k\tau/2}}{\tau} - k \int_{\tau/2}^{\infty} \frac{e^{-k\tau}}{\tau^2} d\tau \right\} \quad (1)$$

From the CRC Handbook of Physics and Chemistry :

$$\int_{-\infty}^1 \frac{e^{-yu}}{u} du = \gamma + \ln y - y + \frac{y^2}{2.2!} - \frac{y^3}{3.3!} + \frac{y^4}{4.4!} - \dots$$

$$\text{where } \gamma = 0.577$$

To solve $\int_{\tau/2}^{\infty} \frac{e^{-k\tau}}{\tau} d\tau$ let $k\tau = \phi \Rightarrow \phi_0 = \frac{k\tau}{2}$

$$d\tau = \frac{d\phi}{k}$$

At $\tau = \frac{\tau}{2} \quad \phi = \phi_0 = \frac{k\tau}{2} = 1$

Substituting :

$$\int_{\tau/2}^{\infty} \frac{e^{-k.t}}{t} dt = \int_1^{\infty} \frac{e^{-\phi}}{(\phi/k)k} d\phi = \int_1^{\infty} \frac{e^{-\phi}}{\phi} d\phi = - \int_{-\infty}^1 \frac{e^{-\phi}}{\phi} d\phi$$

Here $y = 1$

$$\int_{\tau/2}^{\infty} \frac{e^{-y}}{t} dt \equiv - \left[\gamma + \ln(y) - y + \frac{y^2}{2 \cdot 2!} - \frac{y^3}{3 \cdot 3!} + \frac{y^4}{4 \cdot 4!} \right]$$

Note: Series is truncated after y^4

$$\int_{\tau/2}^{\infty} \frac{e^{-k.t}}{t} dt \equiv - \left[0.577 + 0 - y + \frac{1}{4} - \frac{1}{18} + \frac{1}{96} \right] = 0.218$$

Equation (1) becomes :

$$\bar{X} = 1 - e^{-k.\tau/2} + \frac{k.\tau}{2} e^{-k.\tau/2} - \frac{k^2.\tau^2}{4} (0.218)$$

$$\bar{X} = 1 - e^{-1} + e^{-1} - 0.218$$

$$\therefore \bar{X} = 1 - 0.218 = 0.782$$

Problem P13-11B (old manual solution)

Turbulent velocity profile is given by :

$$u = u_{\max} \left(1 - \frac{r}{R} \right)^{1/7}$$

Fraction of fluid between r and $r + dr$:

$$\frac{dv}{v_0} = \frac{2.\pi.r}{v_0} r.dr.u(r)$$

To find $E(t)$ which is the fraction of fluid between time t and $t + dt$, we need to relate r and t :

$$u_{avg} = \frac{\int_0^R 2\pi.r.u(r).dr}{\int_0^R 2\pi.r.dr} = \frac{2.\pi \int_0^R r.u_{\max} \left(1 - \frac{r}{R} \right)^{1/7} dr}{\pi.R^2}$$

P13-11 cont'd

Let $X = 1 - r/R \quad \Rightarrow \quad r = (1 - X) R \quad dr = -R dX$

At $r = 0 \quad X = 1$
 $r = R \quad X = 0$

$$u_{avg} = \frac{2}{R^2} \cdot u_{max} \int_1^0 X^{1/7} R(1-X)(-R) dX = -2 \cdot u_{max} \int_1^0 (X^{1/7} - X^{8/7}) dX$$

$$u_{avg} = 2 \cdot u_{max} \left[\frac{7}{8} X^{8/7} - \frac{7}{15} X^{15/7} \right]_1^0 = (2 \cdot u_{max})(7) \left(\frac{15-8}{120} \right) = \frac{49}{60} u_{max}$$

But $u_{avg} = \frac{u_o}{\pi \cdot R^2}$

$$u_{max} = \frac{60}{49} \frac{u_o}{\pi \cdot R^2}$$

then $u(r) = \frac{60}{49} \frac{u_o}{\pi \cdot R^2} \left(1 - \frac{r}{R} \right)^{1/7}$

$$t = \frac{L}{u(r)} = \frac{49}{60} \frac{\pi \cdot R^2 L}{u_o} \frac{1}{\left(1 - \frac{r}{R} \right)^{1/7}} = \frac{49}{60} \frac{\tau}{\left(1 - \frac{r}{R} \right)^{1/7}}$$

where $\tau = \frac{\pi \cdot R^2 L}{u_o}$

$$dt = \frac{49}{60} \tau \left[-\frac{1}{7} \frac{1}{\left(1 - \frac{r}{R} \right)^{8/7}} \left(-\frac{1}{R} \right) dr \right] = \frac{7}{60} \frac{\tau}{R} \frac{1}{\left(1 - \frac{r}{R} \right)^{8/7}} dr$$

$$dt = \frac{7}{60} \frac{\tau}{R} \left[\frac{1}{\left(1 - \frac{r}{R} \right)^{8/7}} \left(\frac{49}{60} \tau \right)^8 \right] \left(\frac{60}{49 \cdot \tau} \right)^8 = \frac{0.5896}{R \tau^7} t^8 dr$$

Also

$$\left(1 - \frac{r}{R}\right)^{1/7} = \frac{49}{60} \frac{\tau}{R}$$

or

$$r = R \left[1 - \left(\frac{49}{60} \frac{\tau}{R} \right)^7 \right]$$

Substituting

$$\frac{dv}{v} = \frac{2\pi}{v} \left(\frac{L}{t} \right)^4 \left[1 - \left(\frac{49}{60} \frac{\tau}{t} \right)^7 \right] \frac{R\tau^7}{0.5896t^8} dt$$

$$E(t) = 3392213 \frac{\tau^8}{t^9} \left[1 - \left(\frac{49}{60} \frac{\tau}{t} \right)^7 \right]$$

Checking: $\int_0^{\frac{49}{60}\tau} E(t) dt = \int_{\frac{49}{60}\tau}^{\infty} E(t) dt$

$$X = \frac{49}{60} \frac{\tau}{t} \Rightarrow t = \frac{49}{60} \frac{\tau}{X}$$

$$t = \frac{49}{60} \tau \rightarrow X = 1$$

Let

and

$$dt = -\frac{49}{60} \frac{\tau}{X^2} dX$$

$$t = \infty \rightarrow X = 0$$

$$\therefore \int_0^{\frac{49}{60}\tau} E(t) dt = \int_1^0 339213 \frac{\tau^8}{\left(\frac{49}{60} \frac{\tau}{X} \right)^9} [1 - X^7] - \left(\frac{49}{60} \frac{\tau}{X^2} \right) dX$$

$$\int_0^{\frac{49}{60}\tau} E(t) dt = -339213 \left(\frac{60}{49} \right)^8 \int_1^0 X^7 (1 - X^7) dX$$

$$\int_0^{\frac{49}{60}\tau} E(t) dt = -339213 \left(\frac{60}{49} \right)^8 \left[\frac{X^8}{8} - \frac{X^{15}}{15} \right]_1^0 = -339213 \left(\frac{60}{49} \right)^8 \left(-\frac{7}{120} \right)$$

$$\int_0^{\frac{49}{60}\tau} E(t) dt = 100$$

We have

$$u_{\max} = \frac{60}{49} \frac{u_0}{\pi R^2} \Rightarrow u_0 = \frac{49\pi R^2}{60} u_{\max}$$

$$u_0 = \frac{49\pi (10\text{dm})^2}{60} (10\text{dm/s}) = 2565.63\text{dm}^3/\text{s}$$

$$\tau = \frac{\pi R^2 L}{u_0} = \frac{(\pi)(10\text{dm})^2 (100\text{dm})}{2565.63\text{dm}^3/\text{s}} = 12.245\text{s}$$

PFR

$$\frac{dC_A}{dt} = -k \cdot C_A$$

$$L\eta \frac{C_A}{C_{A0}} = -k \cdot t$$

$$1 - X = \frac{C_A}{C_{A0}} = e^{-k \cdot t}$$

$$X = 1 - e^{-k \cdot t} = 1 - e^{-0.1t}$$

$$\bar{X} = \int_0^{\frac{49}{60} 12.245} X(t) E(t) dt = 3.39213 (12.245)^8 \int_0^{\frac{49}{60} 12.245} \left\{ 1 - \left[\frac{(49)(12.245)}{(60)t^9} \right]^7 \right\} \frac{(1 - e^{-0.1t})}{t^9} dt$$

$$\bar{X} = 1.7145e9 \int_{10}^{\frac{49}{60} 12.245} \left\{ 1 - \left[\frac{10}{t} \right]^7 \right\} \frac{(1 - e^{-0.1t})}{t^9} dt = 0.70$$

Problem P13-12g (old manual solution)

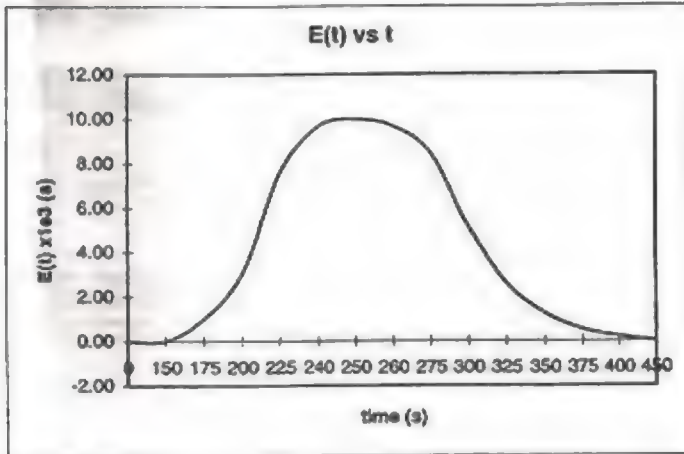
t	C	E(t)	F(t)	t ₁ E(t)	(t-t _m) ²	E(t) (t-t _m) ²	1 - (e ^{-k_t})	(1 - (e ^{-k_t}))E(t)	1/(1+k _t Co.)	E(t)/X(t)
sec	g/l	sec		(x1000)	(x1000)		k _t	(x1000)		
150	0	0	0	0	-	0	0	0	0	0
175	1	1.03		180.25	7.482	7.71	0.866	0.982	134	0.318
200	3	3.08	0.06	616	3.78	11.64	0.9	2.772	148	0.456
210	4.5	4.62		970.2	2.65	12.24	0.91	4.204	153	0.71
220	6.3	6.47		1423.4	1.72	11.13	0.92	5.952	159	1.03
230	8.5	8.74		2010.2	0.99	8.65	0.93	8.128	163	1.43
240	9.4	9.66		2318.4	0.462	4.46	0.94	9.080	169	1.63
250	9.7	9.97		2492.5	0.132	1.32	0.944	9.412	174	1.73
260	9.4	9.66	0.324	2511.6	0.002	0.02	0.95	9.177	178	1.72
270	8.6	8.44	0.422	2278.8	0.072	0.61	0.955	8.060	183	1.62
280	7.6	7.81		2186.8	0.342	2.67	0.96	7.498	188	1.47
290	6.3	6.47	0.768	1876.3	0.812	5.25	0.964	6.237	192	1.24
300	5	5.14	0.826	1542	1.482	7.62	0.968	4.976	196	1.01
325	2.5	2.57		835.25	4.03	10.36	0.976	2.508	207	0.532
350	1.2	1.23	0.976	430.5	7.83	9.63	0.982	1.208	217	0.266
400	0.2	0.21		84	19.18	4.03	0.99	0.208	235	0.049
450	0	0	1	0	-	0	-	0	-	0

33.3

Problem P13-12(old manual solution)

Part (a)

$$\int_0^{\infty} C(t)dt = 0.973 \text{ gm. s / dm}^3$$



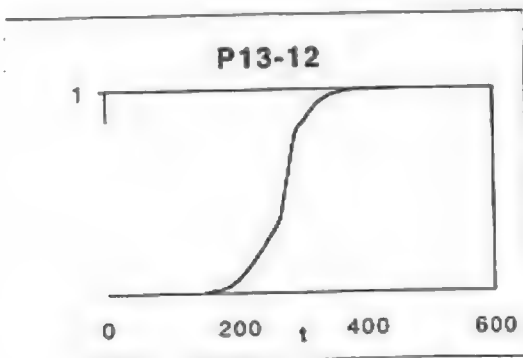
Part (b)

To find the fraction spending between 230 and 270 s, use Simpson's rule for points between 230 and 270 s :

$$\int_{230}^{270} E(t)dt = \frac{10}{3} [8.74 + 4(9.66 + 9.66) + 2(9.97) + 8.84] \times 10^{-3}$$

$$\int_{230}^{270} E(t)dt = 0.382$$

Part (c)



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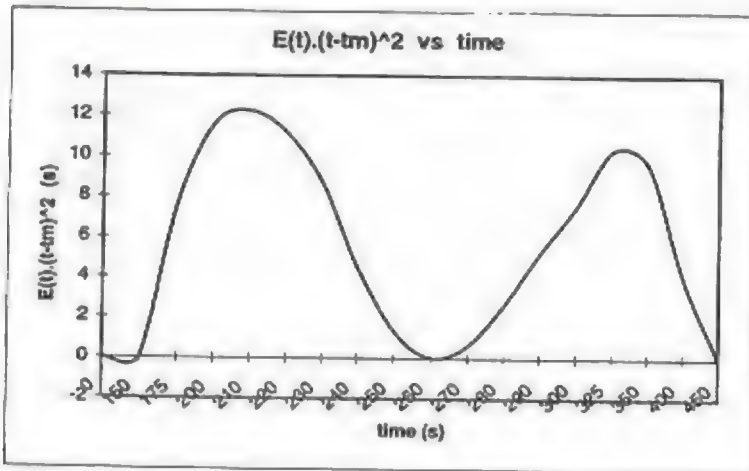
Part (d)

The fraction spending less than 250 s is 0.422

Part (e)

Mean residence time = $t_m = \int_0^{\infty} t \cdot E(t) dt = 273$ s from polynomial fitting

Part (f)



Part (g)

$$\sigma^2 = \int_0^{\infty} (t - t_m)^2 E(t) dt = 1832 \text{ by polynomial fitting}$$

The standard deviation = 42.81 s

Part (h)

The $E(t)$ graph demonstrates good symmetry about the mean time $t_m = 260$ s. The model suggested the reactor is a plug flow reactor with $\tau = 250$ s.

Part (i)

For segregation model : $\bar{X} = \int_0^{\infty} X(t) E(t) dt$

P13-12 cont'd

For first order $X(t) = 1 - e^{-kt}$ with $k = 0.0115 /s$

Gives $\bar{x} = 94.5 \%$

Part (j)

For second order reaction : $\frac{dC}{dt} = -k \cdot C^2 \Rightarrow -\frac{1}{C} + \frac{1}{C_0} = -k \cdot t$

$$\frac{1}{C} = \frac{1}{C_0} + k \cdot t$$

$$C = \frac{C_0}{1 + k \cdot C_0 \cdot t}$$

$$1 - X = \frac{1}{1 + k \cdot C_0 \cdot t}$$

$$X = \frac{k \cdot C_0 \cdot t}{1 + k \cdot C_0 \cdot t}$$

$$\bar{X} = k \cdot C_0 \int_0^{\bar{t}} \frac{t}{1 + k \cdot C_0 \cdot t} E(t)$$

where $C_0 = 0.01 \text{ mol/dm}^3$ $k = 10.55/60 = 0.1758 \text{ mol/dm}^3\text{s}$

gives $\bar{x} = 0.313$

Problem P13-13_B

The elementary gas phase reaction : $A + B \rightarrow C$ in a CSTR

$F_C = 20 \text{ kg/s}$; $V_0 = 1 \text{ m}^3$; $C_{A0} = 0.4 \text{ mol/dm}^3$; $v_0 = 10 \text{ dm}^3/\text{s}$;

$k_d = 0.06 /s$; $k = 0.03 \text{ dm}^6/\text{mol.s.g}$; $\tau_c = 200/20 = 10 \text{ s}$

Second order decay : $\frac{da}{dt} = -k_d \cdot a^2 \Rightarrow a = \frac{1}{1 + k_d \cdot t}$

Part (a)

P13-13

cont'd

Mean activity existing in the reactor :

$$\bar{a} = \int_0^{\infty} a(t) \cdot E(t) dt$$

$$\bar{a} = \frac{1}{\tau} \int_0^{\infty} \frac{e^{-t/\tau}}{1 + k_d t} dt = \frac{1}{10} \int_0^{\infty} \frac{e^{-t/10}}{1 + 0.06t} dt$$

t	$\frac{e^{-t/10}}{1 + 0.06t}$
0	1
5	0.467
10	0.229
15	0.117
20	0.0615
25	0.0328
30	0.0178
35	0.0097
40	0.0054
45	0.0030
50	0.0017
55	0.00095
60	0.00054
65	0.00031

Use Simpson's rule to evaluate the integral : $\bar{a} = \frac{6.9219}{10} = 0.6922$

Part (b)

The mean activity of the catalyst in the reactor is the same as that at the exit. In the case of non-linear rate problem the mean activity calculated from residence time distribution will give an upper bound for order greater than unity and lower bound for order less than unity.

The actual value of mean activity can be calculated using population balance technique. (see Joshi, P.A., PhD thesis, Dept Chemical Engineering, IIT, Bombay, 1985)

Part (c)

Assuming micromixing : $W = \frac{F_{AO}X}{-r_{AO} \bar{a}}$

or $W_0 X = k \cdot C_{AO} \frac{(1-X)^2}{(1+\varepsilon \cdot X)^2} \bar{a} \cdot W$

$\varepsilon = -0.5$

Checking units : $\text{dm}^3/\text{s} = \text{dm}^6/\text{mol.s.g} \times \text{mol.g}/\text{dm}^3$

$\text{dm}^3/\text{s} = \text{dm}^3/\text{s}$ OK

$10X = \frac{(0.03) \cdot (0.04) \cdot (1-X)^2 \cdot (0.6922) \cdot (2 \times 10^5)}{(1-0.5X)^2}$

eqn (1)

$X = 16.613 \frac{(1-X)^2}{(1-0.5X)^2} \Rightarrow X = 0.87$

Part (d)

Assuming segregation model :

$-r_A = -\frac{1}{W} \frac{dN_A}{dt} = \frac{N_{AO}}{W} \frac{dX}{dt} = k \cdot C_{AO}^2 \frac{(1-X)^2}{(1+\varepsilon \cdot X)^2} a(t)$

$\frac{C_{AO} \cdot V_0}{W} \frac{dX}{dt} = k \cdot C_{AO}^2 \frac{(1-X)^2}{(1+\varepsilon \cdot X)^2} \cdot \frac{1}{1+k_d \cdot t}$

$\int_0^X \frac{(1-X)^2}{(1+\varepsilon \cdot X)^2} \frac{dX}{dt} = \frac{k \cdot C_{AO} \cdot W}{k_d \cdot V_0} L_n(1+k_d \cdot t)$

$2\varepsilon(1+\varepsilon)L_n(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon)^2 X}{(1-X)} = \frac{k \cdot C_{AO} \cdot W}{k_d \cdot V_0} L_n(1+k_d \cdot t)$

$-0.5L_n(1-X) + 0.25X + \frac{0.25X}{1-X} = 4L_n(1-0.06t)$

P13-13 **cont'd**

$$\bar{X} = \int_0^{\infty} X(t)E(t)dt$$

Do it numerically.

Part (e)

$X = 0.75$ Use eqn (1) where W is unknown :

$$(10)(0.75) = \frac{(0.03).(0.04).(1 - (0.75))^2(0.6922).(W)}{(1 - 0.5(0.75))^2}$$

$$W = 56,432g$$

Part (f)

$\tau = 2 \text{ s}$

$$\bar{a} = \frac{1}{2} \int_0^{\infty} \frac{e^{-t/\tau}}{1 + 0.06t} dt = \frac{1}{2} \int_0^{\infty} f(t) dt \quad \text{where} \quad \frac{e^{-t/\tau}}{1 + 0.06t}$$

t	f(t)
0	1
1	0.5722
2	0.3285
3	0.1891
4	0.1091
5	0.06314
6	0.03661
7	0.02127
8	0.01238
9	0.00721
10	0.00421

Use Simpson's rule to evaluate the integral :

$$\bar{a} = \frac{1.7964}{2} = 0.8982$$

$$10X = \frac{(0.03).(0.04).(1 - X)^2(0.8982).(2 \times 10^5)}{(1 - 0.5X)^2}$$

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$$X = 21.56 \frac{(1-X)^2}{(1-0.5X)^2}$$

$$X = 0.89$$

does not change very much.

Part (g)

For first order decay :

$$\frac{da}{dt} = -k_d \cdot a$$

$$a = a_0 \cdot e^{-k_d t}$$

$$\bar{a} = \frac{1}{\tau_c} \int_0^{\infty} e^{-k_d t} e^{t/\tau_c} dt = -\frac{1}{\tau_c} \left[\frac{\exp\left\{-\left(k_d + \frac{1}{\tau_c}\right)t\right\}}{k_d + \frac{1}{\tau_c}} \right]_0^{\infty}$$

$$\bar{a} = \frac{1}{1 + k_d \cdot \tau_c} = \frac{1}{1 + (0.06) \cdot (10)} = 0.625$$

$$10X = \frac{(0.03) \cdot (0.04) \cdot (1-X)^2 \cdot (0.625) \cdot (2 \times 10^5)}{(1-0.5X)^2}$$

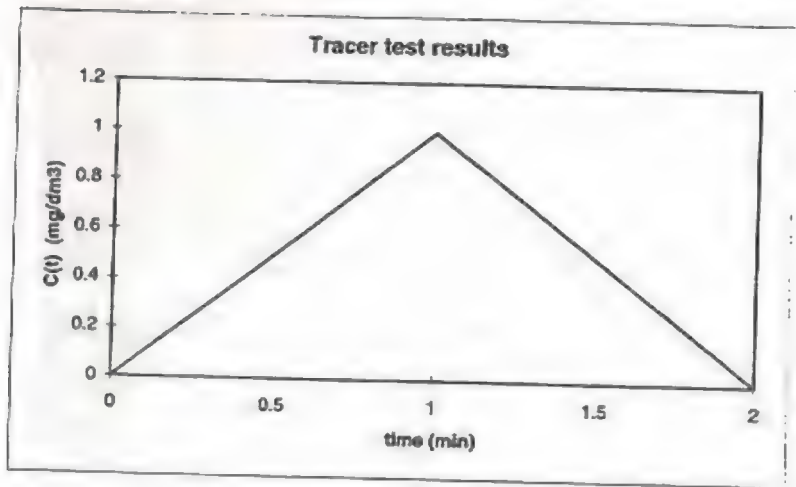
$$X = 15 \frac{(1-X)^2}{(1-0.5X)^2}$$

$$X = 0.86$$

$$(10)(0.75) = \frac{(0.03) \cdot (0.04) \cdot (1-0.75)^2 \cdot (0.625) \cdot (W)}{(1-0.5(0.75))^2}$$

$$W = 62,500g$$

Problem P13-14



Part (a)

Liquid phase, segregation model, second order, non ideal GSTR, adiabatic

$$\bar{X} = \int_0^{\infty} X(t, T) \cdot E(t) dt = 0.67$$

$$E(t) = \frac{C(t)}{\int_0^{\infty} C(t) dt} \quad \text{but} \quad \int_0^{\infty} C(t) dt = 1 \text{ mg} \cdot \text{min} / \text{dm}^3$$

$$E(t) = \text{IF } (t \leq 1) \text{ THEN } (t) \text{ ELSE } (\text{IF } (t \geq 2) \text{ THEN } (0) \text{ ELSE } (2 - t))$$

$$\text{For a batch globule: } C_{A0} \frac{dX}{dt} = -r_A$$

$$-r_A = k \cdot C_A^2$$

$$C_A = C_{A0}(1 - X)$$

$$\frac{dX}{dt} = k \cdot C_{A0} \cdot (1 - X)^2$$

$$\text{where } C_{A0} = 2 \text{ mol} / \text{dm}^3$$

$$k(T) = 0.5 \cdot \exp \left[\frac{E_a}{8.314} \left(\frac{1}{300} - \frac{1}{T} \right) \right]$$

13-41

$$T = T_0 + \frac{-\Delta H_{rx} \cdot X}{C_{ps} + \Delta C_p \cdot X}$$

where

$$C_{ps} = \sum \theta_i C_{pi} = C_{pa} + 0 = 50 \text{ J/mol.K}$$

$$\Delta C_p = 1/2 C_{pb} - C_{pa} = 100/2 - 50 = 0$$

$$T = 300 + 150X$$

Iterate with E_a , using the ODE solver for values of $X(t, T)$ and substitute these into the polynomial regression to evaluate the integral $\bar{X} = \int_0^1 X(t, T) \cdot E(t) dt = 0.67$

When the evaluated integral $\bar{x} = 0.67$ then the E_a is correct.

P13-14

Equations:

$$d(x)/d(t) = k \cdot c_{ao} \cdot (1-x)^2$$

$$c_{ao} = 2$$

$$T = 300 + (150 \cdot x)$$

$$E1 = t$$

$$E2 = 2 - t$$

$$E_a = 10000$$

$$k = 5 \cdot \exp((E_a / 8.314) \cdot ((1/300) - (1/T)))$$

$$E = \text{if}(t \leq 1) \text{ then}(E1) \text{ else}(E2)$$

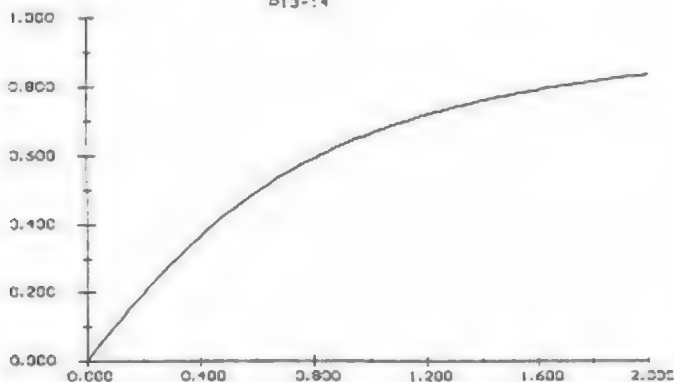
$$t_0 = 0, \quad t_f = 2$$

Initial value

0

$$\frac{dX}{dt}$$

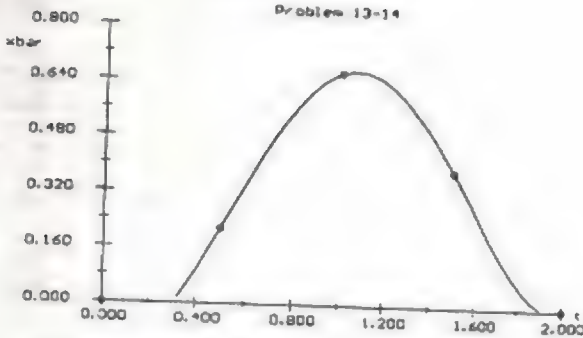
-x



#	t	C	E	X	xbar
1	0	0	0	0	0
2	0.5	0.5	0.5	0.43366	0.21683
3	1	1	1	0.6637	0.6637
4	1.5	0.5	0.5	0.7741	0.38705
5	2	0	0	0.8336	0

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P13-14 cont'd



$$R(t) = 6.50026 \times 10^{-11} - 1.21943 t + 5.23945 t^2 - 4.40477 t^3 + 1.04445 t^4$$

An activation energy E_a of 10000 J/mol gives approximately the correct mean conversion, $\bar{x} = 0.67$. Inaccuracy lies in the polynomial fit and hence the integral area.

Part (b)

Parallel reactions, isothermal, segregation model

batch globules

$$\frac{dC_A}{dt} = r_A = r_{A1} + r_{A2} = -k_{1A}C_A^2 - k_{2C}C_AC_B$$

$$\frac{dC_B}{dt} = r_B = -r_{A1} + r_{A2} = k_{1A}C_A^2 - k_{2C}C_AC_B$$

$$\frac{dC_C}{dt} = r_C = -r_{A2} = k_{2C}C_AC_B$$

exit concentrations

$$\frac{dC_{Abar}}{dt} = C_A E(t)$$

$$\frac{dC_{Bbar}}{dt} = C_B E(t)$$

$$\frac{dC_{Cbar}}{dt} = C_C E(t)$$

$$E(t) = \text{IF } (t \leq 1) \text{ THEN } (t) \text{ ELSE } (\text{IF } (t \geq 2) \text{ THEN } (0) \text{ ELSE } (2 - t))$$

13-43

P13-14 cont'd

selectivity $S = \frac{C_{Bbar}}{C_{Cbar}} \quad (= 2.38)$

Iteration with k_{2C} until $S = 2.38$ gives $k_{2C} = 0.3755 \text{ dm}^3/\text{mol} \cdot \text{min}$

Problem P13-14(b)

Equations:

$$d(Ca)/dt = (-k_{1a} \cdot (Ca^2)) + (k_{2a} \cdot Ca \cdot Cb)$$

$$d(Cb)/dt = (k_{1a} \cdot (Ca^2)) - (k_{2a} \cdot Ca \cdot Cb)$$

$$d(Cc)/dt = k_{2a} \cdot Ca \cdot Cb$$

$$d(Cabar)/dt = Ca \cdot E$$

$$d(Cbbar)/dt = Cb \cdot E$$

$$d(Ccbar)/dt = Cc \cdot E$$

$$k_{1a} = 0.2$$

$$k_{2a} = 0.3755$$

$$E = \text{if}(t \leq 1) \text{ then}(t) \text{ else}(\text{if}(t \geq 2) \text{ then}(0) \text{ else}(2-t))$$

$$S = C_{Bbar} / (C_{Cbar} + 0.000001)$$

$$t_0 = 0. \quad t_f = 4$$

Problem P13-14(b)

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	4	0	4
Ca	2	2	1.32783	1.32783
Cb	0	0.672165	0	0.672165
Cc	0	1.1095	0	1.1095
Cabar	0	1.58256	0	1.58256
Cbbar	0	0.417439	0	0.417439
Ccbar	0	0.175374	0	0.175374
k _{1a}	0.2	0.2	0.2	0.2
k _{2a}	0.3755	0.3755	0.3755	0.3755
E	0	1	0	0
S	0	33.117	0	2.38027

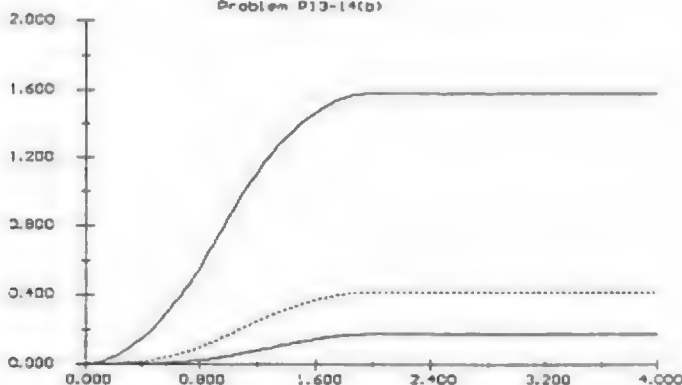
Problem P13-14(b)

KEY:

— Cabar

... Cbbar

— Ccbar



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Problem P13-16_B

Multiple parallel reactions, isothermal

$$E(t) = 0.0279693 - 0.0008527 t + 1.2778e-5 t^2 - 1.0661e-7 t^3 + 4.5747e-10 t^4 - 7.73108e-13 t^5$$

$$k_1 = 5.0 \text{ m}^6/\text{kmol}^2\text{min}, \quad k_2 = 2.0 \text{ m}^3/\text{kmol}\cdot\text{min}, \quad k_3 = 10 \text{ m}^6/\text{kmol}^2\text{min}, \quad k_4 = 5.0 \text{ m}^2/\text{kmol}^{2/3}\text{min}$$

Part (a)

Segregated model

$$\frac{dC_A}{dt} = -k_1 C_A C_B^2 - k_2 C_A C_B - \frac{2}{3} k_4 C_C C_A^{2/3}$$

$$\frac{dC_B}{dt} = -1.25 k_1 C_A C_B^2 - 0.75 k_2 C_A C_B - k_3 C_B C_C^2$$

$$\frac{dC_C}{dt} = k_1 C_A C_B^2 - 2 k_3 C_C^2 C_B - k_4 C_C C_A^{2/3}$$

$$\frac{dC_D}{dt} = 1.5 k_1 C_A C_B^2 + 1.5 k_2 C_A C_B + k_4 C_C C_A^{2/3}$$

$$\frac{dC_E}{dt} = 0.5 k_2 C_A C_B + \frac{5}{6} k_4 C_C C_A^{2/3}$$

$$\frac{dC_F}{dt} = 2 k_3 C_C^2 C_B$$

$$\frac{d\bar{C}_A}{dt} = C_A E(t)$$

$$\frac{d\bar{C}_B}{dt} = C_B E(t)$$

$$\frac{d\bar{C}_C}{dt} = C_C E(t)$$

$$\frac{d\bar{C}_D}{dt} = C_D E(t)$$

$$\frac{d\bar{C}_E}{dt} = C_E E(t)$$

$$\frac{d\bar{C}_F}{dt} = C_F E(t)$$

$$S_{CD} = \frac{\bar{C}_C}{\bar{C}_D}$$

$$S_{DE} = \frac{\bar{C}_D}{\bar{C}_E}$$

$$S_{EF} = \frac{\bar{C}_E}{\bar{C}_F}$$

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P13-16 cont'd

Problem P13-16

<u>Equations:</u>	<u>Initial value</u>
$d(Ca)/d(t) = \{-k_1 \cdot Ca \cdot (Cb^2)\} - \{k_2 \cdot Ca \cdot Cb\} - \{(2/3) \cdot k_4 \cdot Cc \cdot (Ca^{(2/3)})\}$	0.05
$d(Cb)/d(t) = \{-1.25 \cdot k_1 \cdot Ca \cdot (Cb^2)\} - \{0.75 \cdot k_1 \cdot Ca \cdot Cb\} - \{k_3 \cdot Cb \cdot (Cc^2)\}$	0.05
$d(Cc)/d(t) = \{k_1 \cdot Ca \cdot (Cb^2)\} - \{2 \cdot k_3 \cdot Cb \cdot (Cc^2)\} - \{k_4 \cdot Cc \cdot (Ca^{(2/3)})\}$	0
$d(Cd)/d(t) = \{1.5 \cdot k_1 \cdot Ca \cdot (Cb^2)\} + \{1.5 \cdot k_2 \cdot Ca \cdot Cb\} + \{k_4 \cdot Cc \cdot (Ca^{(2/3)})\}$	0
$d(Ce)/d(t) = \{0.5 \cdot k_2 \cdot Ca \cdot Cb\} + \{(5/6) \cdot k_4 \cdot Cc \cdot (Ca^{(2/3)})\}$	0
$d(Cf)/d(t) = \{2 \cdot k_3 \cdot Cb \cdot (Cc^2)\}$	0
$d(Cabar)/d(t) = E \cdot Ca$	0
$d(Cbbar)/d(t) = E \cdot Cb$	0
$d(Ccbar)/d(t) = E \cdot Cc$	0
$d(Cdbar)/d(t) = E \cdot Cd$	0
$d(Cebar)/d(t) = E \cdot Ce$	0
$d(Cfbar)/d(t) = E \cdot Cf$	0

$k_1=5$

$k_2=2$

$k_4=5$

$k_3=10$

$E=0.0279693 - (0.000852735 \cdot t) + \{(1.2778e-5) \cdot (t^2)\} - \{(1.0661e-7) \cdot (t^3)\} + \{(4.5747e-10) \cdot (t^4)\} - \{(7.73108e-13) \cdot (t^5)\}$

$Scd=Ccbar/(Cdbar+0.000000001)$

$Sde=Cdbar/(Cebbar+0.000000001)$

$Sef=Cebbar/(Cfbar+0.00000000001)$

$t_0 = 0, \quad t_f = 200$

Problem P13-16

<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
t	0	200	0	200
Ca	0.05	0.05	0.0217543	0.0217543
Cb	0.05	0.05	1.7211e-09	1.7211e-09
Cc	0	0.000418278	0	1.42227e-18
Cd	0	0.0423686	0	0.0423686
Ce	0	0.0141226	0	0.0141226
Cf	0	4.49497e-07	0	4.49497e-07
Cabar	0	0.0263679	0	0.0263679
Cbbar	0	0.00826231	0	0.00826231
Ccbar	0	6.95492e-05	0	6.95492e-05
Cdbar	0	0.0355547	0	0.0355547
Cebbar	0	0.0118166	0	0.0118166
Cfbar	0	4.15583e-07	0	4.15583e-07
k1	5	5	5	5
k2	2	2	2	2
k4	5	5	5	5
k3	10	10	10	10
E	0.0279693	0.0279693	0.00021974	0.00021974
Scd	0	0.0703057	0	0.00195612
Sde	0	3.35056	0	3.00888
Sef	0	206571	0	28433.1

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Exit concentrations :

$$\bar{C}_A = 0.026 \text{ mol} / \text{dm}^3$$

Selectivities

$$\bar{C}_B = 0.008$$

$$S_{CD} = 0.00196$$

$$\bar{C}_C = 6.955e-5$$

$$S_{DE} = 3.009$$

$$\bar{C}_D = 0.036$$

$$S_{EF} = 28433$$

$$\bar{C}_E = 0.012$$

$$\bar{C}_F = 4.156e-7$$

Part (b)

Maximum mixedness model

$$E(t) = 0.0279693 - 0.0008527\lambda + 1.2778e-5\lambda^2 - 1.0661e-7\lambda^3 + 4.5747e-10\lambda^4 - 7.73108e-13\lambda^5$$

and $\lambda = t_f - z$, where $z = t$, $t_f = 200$ min (extent of $E(t)$).

$$\frac{dC_A}{dz} = r_A - \left((C_A - C_{Ao}) \frac{E(\lambda)}{1 - F(\lambda)} \right)$$

$$\text{and } r_A = \left(-k_1 \cdot C_A \cdot C_B^2 - k_2 \cdot C_A \cdot C_B - \frac{2}{3} k_4 \cdot C_C \cdot C_A^{2/3} \right)$$

and so on for the other species.

$$\frac{dF(\lambda)}{dz} = -E(\lambda) \quad \text{gives } F(\lambda)$$

Problem P13-16

Equations:

Initial value

$$d(Ca)/d(z) = \{ (-k_1 \cdot Ca \cdot (Cb^2)) - (k_2 \cdot Ca \cdot Cb) - ((2/3) \cdot k_4 \cdot Cc \cdot (Ca^{2/3})) - ((Ca - Cao) \cdot E / (1 - F)) \} \quad 0.05$$

$$d(Cb)/d(z) = \{ (-1.25 \cdot k_1 \cdot Ca \cdot (Cb^2)) - (0.75 \cdot k_1 \cdot Ca \cdot Cb) - (k_3 \cdot Cb \cdot (Cc^2)) - ((Cb - Cbo) \cdot E / (1 - F)) \} \quad 0.05$$

$$d(Cc)/d(z) = \{ (k_1 \cdot Ca \cdot (Cb^2)) - (2 \cdot k_3 \cdot Cb \cdot (Cc^2)) - (k_4 \cdot Cc \cdot (Ca^{2/3})) - (Cc \cdot E / (1 - F)) \} \quad 0$$

$$d(F)/d(z) = -E \quad 0.99999$$

$$d(Cd)/d(z) = \{ (1.5 \cdot k_1 \cdot Ca \cdot (Cb^2)) + (1.5 \cdot k_2 \cdot Ca \cdot Cb) + (k_4 \cdot Cc \cdot (Ca^{2/3})) - (Cd \cdot E / (1 - F)) \} \quad 0$$

$$d(Ce)/d(z) = \{ (0.5 \cdot k_2 \cdot Ca \cdot Cb) + ((5/6) \cdot k_4 \cdot Cc \cdot (Ca^{2/3})) - (Ce \cdot E / (1 - F)) \} \quad 0$$

$$d(Cf)/d(z) = \{ (2 \cdot k_3 \cdot Cb \cdot (Cc^2)) - (Cf \cdot E / (1 - F)) \} \quad 0$$

$$k_3 = 10$$

$$k_1 = 5$$

$$k_2 = 2$$

$$k_4 = 5$$

13-47

$$C_{ao}=0.05$$

$$C_{bo}=0.05$$

$$\text{lam}=200-z$$

$$S_{cd}=C_c/(C_d+0.0000000001)$$

$$S_{de}=C_d/(C_e+0.0000000001)$$

$$S_{ef}=C_e/(C_f+0.0000000001)$$

$$E=0.02797-(0.000852735*\text{lam})+((1.2778e-5)*(\text{lam}^2))-((1.0661e-7)*(\text{lam}^3))+((4.5747e-10)*(\text{lam}^4))-((7.73108e-13)*(\text{lam}^5))$$

$$z_0 = 0, \quad z_f = 200$$

Problem P13-16

Variable	Initial value	Maximum value	Minimum value	Final value
z	0	200	0	200
Ca	0.05	0.05	0.0262434	0.0282525
Cb	0.05	0.05	0.00690604	0.0101378
Cc	0	0.000318211	0	2.9267e-05
F	0.99999	0.99999	-0.00157133	-0.00157133
Cd	0	0.035635	0	0.0326212
Ce	0	0.0118713	0	0.0108591
Cf	0	2.10543e-07	0	7.98503e-09
k3	10	10	10	10
k1	5	5	5	5
k2	2	2	2	2
k4	5	5	5	5
Cao	0.05	0.05	0.05	0.05
Cbo	0.05	0.05	0.05	0.05
lam	200	200	0	0
Scd	0	0.0736547	0	0.000897176
Sde	0	3.3725	0	3.00404
Sef	0	1.34311e+06	0	1.34311e+06
E	0.00022044	0.02797	0.00022044	0.02797

Exit selectivities :

$$C_A = 0.028 \text{ mol} / \text{dm}^3$$

$$C_B = 0.010$$

$$C_C = 2.927e-5$$

$$C_D = 0.033$$

$$C_E = 0.011$$

$$C_F = 7.985e-9$$

Selectivities :

$$S_{CD} = 0.0009$$

$$S_{DE} = 3.004$$

$$S_{EF} = 1343110$$

Part (c)

Ideal CSTR

$$t_m = \tau \quad \text{and} \quad E(t) = \frac{e^{-t/\tau}}{\tau}$$

13-48

Mol balances :

$$\frac{dF_A}{dt} = F_{AO} - (-r_A) \quad \text{where } r_A = -k_1 C_A C_B^2 - k_2 C_A C_B - \frac{2}{3} k_4 C_C C_A^{2/3}$$

$$F_{AO} = C_{AO} v_0 = 0.05 * 10 = 0.5 \text{ mol/min} = F_{BO}$$

and so on for the other species.

$$C_A = C_{T0} \frac{F_A}{F_T} \rightarrow \text{etc...}$$

$$C_{T0} = C_{AO} + C_{BO} = 0.05 + 0.05 = 0.1$$

$$F_T = F_A + F_B + F_C + F_D + F_E + F_f$$

Problem P13-16

Equations:

Initial value

$$d(F_A)/d(\tau) = 0.5 * \{ (-k_1 * C_A * (C_B^2)) - (k_2 * C_A * C_B) - ((2/3) * k_4 * C_C * \{ C_A^{(2/3)} \}) \} \quad 0.5$$

$$d(F_B)/d(\tau) = \{ (2 * k_3 * C_B * (C_C^2)) \} \quad 0$$

$$d(F_B)/d(\tau) = 0.5 * \{ (-1.25 * k_1 * C_A * (C_B^2)) - (0.75 * k_1 * C_A * C_B) - (k_3 * C_B * (C_C^2)) \} \quad 0.5$$

$$d(F_C)/d(\tau) = \{ (k_1 * C_A * (C_B^2)) - (2 * k_3 * C_B * (C_C^2)) - (k_4 * C_C * (C_A^{(2/3)})) \} \quad 0$$

$$d(F_D)/d(\tau) = \{ (1.5 * k_1 * C_A * (C_B^2)) + (1.5 * k_2 * C_A * C_B) + (k_4 * C_C * (C_A^{(2/3)})) \} \quad 0$$

$$d(F_E)/d(\tau) = \{ (0.5 * k_2 * C_A * C_B) + ((5/6) * k_4 * C_C * (C_A^{(2/3)})) \} \quad 0$$

$$k_1 = 5$$

$$k_2 = 2$$

$$k_4 = 5$$

$$k_3 = 10$$

$$E = 0.0279693 - (0.000852735 * \tau) + \{ (1.2778e-5) * (\tau^2) \} - \{ (1.0661e-7) * (\tau^3) \} + \{ (4.5747e-10) * (\tau^4) \} - \{ (7.73108e-13) * (\tau^5) \}$$

$$C_{AO} = 0.05$$

$$C_{BO} = 0.05$$

$$F_T = F_A + F_B + F_C + F_D + F_E + F_f$$

$$C_A = 0.1 * F_A / F_T$$

$$C_B = 0.1 * F_B / F_T$$

$$C_C = 0.1 * F_C / F_T$$

$$C_D = 0.1 * F_D / F_T$$

$$C_E = 0.1 * F_E / F_T$$

$$C_f = 0.1 * F_f / F_T$$

$$S_{cd} = \text{if}(\tau < 1) \text{ then } (C_C / (C_D + 0.00001)) \text{ else } (C_C / C_D)$$

$$S_{de} = \text{if}(\tau < 1) \text{ then } (C_D / (C_E + 0.00001)) \text{ else } (C_D / C_E)$$

$$S_{ef} = \text{if}(\tau < 1) \text{ then } (C_E / (C_f + 0.00001)) \text{ else } (C_E / C_f)$$

$$t_0 = 0, \quad t_f = 200$$

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Problem P13-16

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	200	0	200
F _A	0.5	99.3967	0.5	99.3967
F _f	0	6.07003e-07	0	6.07003e-07
F _b	0.5	98.5159	0.5	98.5159
F _c	0	0.112878	0	0.112878
F _d	0	1.65498	0	1.65498
F _e	0	0.49522	0	0.49522
k ₁	5	5	5	5
k ₂	2	2	2	2
k ₄	5	5	5	5
k ₃	10	10	10	10
Z	0.0279693	0.0279693	0.00021974	0.00021974
C _{ao}	0.05	0.05	0.05	0.05
C _{bo}	0.05	0.05	0.05	0.05
F _t	1	200.176	1	200.176
C _a	0.05	0.05	0.0496547	0.0496547
C _b	0.05	0.05	0.0492147	0.0492147
C _c	0	5.63893e-05	0	5.63893e-05
C _d	0	0.000826763	0	0.000826763
C _e	0	0.000247393	0	0.000247393
C _f	0	3.03235e-10	0	3.03235e-10
S _{cd}	0	0.0719365	0	0.0682049
S _{de}	0	3.36287	0	3.3419
S _{ef}	0	4.99062e+06	0	815844

Exit concentrations :

$$C_A = 0.050 \text{ mol / dm}^3$$

$$C_B = 0.049$$

$$C_C = 5.639e-5$$

$$C_D = 0.0008$$

$$C_E = 0.0002$$

$$C_F = 3.03e-10$$

Selectivities :

$$S_{CD} = 0.068$$

$$S_{DE} = 3.342$$

$$S_{EF} = 815844$$

Ideal PFR

$$t_m = \tau \quad \text{and} \quad \text{RTD function } E(t) = \delta(t - \tau)$$

$$\frac{dF_A}{dV} = (-r_A) \quad r_A = -k_1 C_A C_B^2 - k_2 C_A C_B - \frac{2}{3} k_4 C_C C_A^{2/3}$$

and so on for the other species.

$$C_A = C_{T0} \frac{F_A}{F_T} \rightarrow \text{etc...}$$

$$C_{T0} = C_{A0} + C_{B0} = 0.05 + 0.05 = 0.1$$

$$F_T = F_A + F_B + F_C + F_D + F_E + F_F$$

Problem P13-16

Equations:

$$d(Ff)/d(V) = -2 \cdot r3b$$

$$d(Pa)/d(V) = r1a + r2a + 2 \cdot r4c/3$$

$$d(Fb)/d(V) = 1.25 \cdot r1a + 0.75 \cdot r2a + r3b$$

$$d(Pc)/d(V) = -r1a + 2 \cdot r3b + r4c$$

$$d(Pd)/d(V) = -1.5 \cdot r1a - 1.5 \cdot r2a - r4c$$

$$d(Pe)/d(V) = -0.5 \cdot r2a - 5 \cdot r4c/6$$

$$P_t = P_a + P_b + P_c + P_d + P_e + P_f$$

$$r1a = -5 \cdot 8 \cdot (Pa/P_t) \cdot (Fb/P_t) \cdot 2$$

$$r2a = -2 \cdot 4 \cdot (Pa/P_t) \cdot (Fb/P_t)$$

$$r4c = -5 \cdot 3.175 \cdot (Pc/P_t) \cdot (Pa/P_t) \cdot (2/3)$$

$$r3b = -10 \cdot 8 \cdot (Pc/P_t) \cdot 2 \cdot (Fb/P_t)$$

$$Ca = 0.1 \cdot Pa/P_t$$

$$Cb = 0.1 \cdot Fb/P_t$$

$$Cc = 0.1 \cdot Pc/P_t$$

$$Cd = 0.1 \cdot Pd/P_t$$

$$Ce = 0.1 \cdot Pe/P_t$$

$$Cf = 0.1 \cdot Pf/P_t$$

$$Scd = Cc / (Cd + 0.00001)$$

$$Sde = Cd / (Ce + 0.00001)$$

$$Sef = Ce / (Cf + 0.00001)$$

$$V_0 = 0, \quad V_f = 10$$

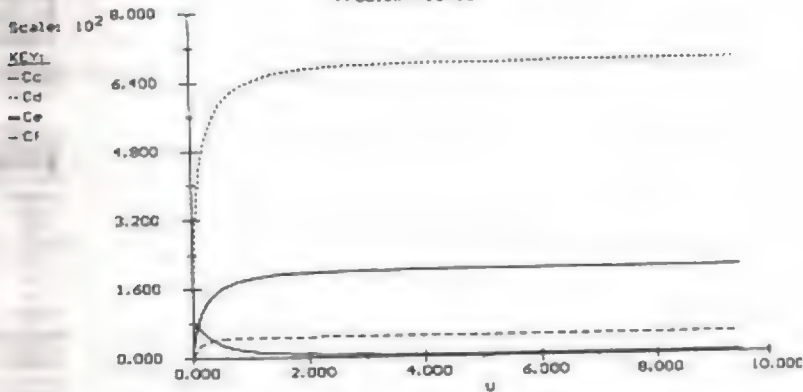
Problem P13-16

Variable	Initial value	Maximum value	Minimum value	Final value
V	0	9.5	0	9.5
Pf	0	0.0518155	0	0.0518155
Pa	0.5	0.5	4.37412e-08	4.37412e-08
Fb	0.5	0.5	0.0716595	0.0716595
Pc	0	0.0812645	0	0.00305004
Pd	0	0.75	0	0.75
Pe	0	0.222567	0	0.222567
Pt	1	1.0992	1	1.09909
r1a	-5	-6.767e-09	-5	-6.767e-09
r2a	-2	-2.0758e-08	-2	-2.0758e-08
r4c	-0	-0	-0.554504	-5.1352e-07
r3b	-0	-0	-0.144083	-4.01674e-05
Ca	0.05	0.05	3.97976e-09	3.97976e-09
Cb	0.05	0.05	0.00651988	0.00651988
Cc	0	0.00779971	0	0.000277506
Cd	0	0.0682381	0	0.0682381

P13-16 cont'd

Ce	0	0.0202501	0	0.0202501
Cf	0	0.00471439	0	0.00471439
Scd	0	0.366108	0	0.00406613
Sde	0	7.03231	0	3.36811
Sef	0	8.0226	0	4.28629

Problem P13-16



Exit concentrations :

Selectivities :

$$C_A = 3.98e-9 \text{ mol / dm}^3$$

$$C_B = 0.0065$$

$$C_C = 0.000277$$

$$C_D = 0.068$$

$$C_E = 0.0202$$

$$C_F = 0.0047$$

$$S_{CD} = 0.004$$

$$S_{DE} = 3.368$$

$$S_{EF} = 4.286$$

Segregation

$$S_{CD} = 0.00196$$

$$S_{DE} = 3.009$$

$$S_{EF} = 28433$$

Maxixmum M

$$S_{CD} = 0.0009$$

$$S_{DE} = 3.004$$

$$S_{EF} = 1343110$$

CSTR

$$S_{CD} = 0.068$$

$$S_{DE} = 3.342$$

$$S_{EF} = 815844$$

PFR

$$S_{CD} = 0.004$$

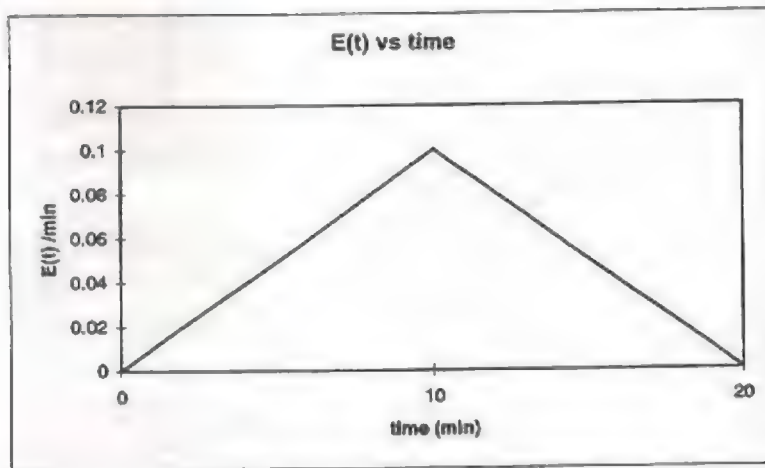
$$S_{DE} = 3.368$$

$$S_{EF} = 4.286$$

S_{EF} for the PFR is very much smaller than for the others, because C_F is not so small at the exit of the PFR in turn due to exit C_C is not so small either. The conversion of C_A in the PFR is virtually complete at the exit of the PFR, hence greater C_C .

13-52

Part (d)



$$E(t) = \text{IF } (t \leq 10) \text{ THEN } (0.01 t) \text{ ELSE } (\text{IF } (t \geq 20) \text{ THEN } (0) \text{ ELSE } (0.2 - 0.01 t))$$

Segregation	Maximum M	CSTR	PFR
$S_{CD} = 0.004$	$S_{CD} = 0.0035$	$S_{CD} = 0.068$	$S_{CD} = 0.004$
$S_{DE} = 3.109$	$S_{DE} = 3.106$	$S_{DE} = 3.342$	$S_{DE} = 3.368$
$S_{EF} = 24078$	$S_{EF} = 41503$	$S_{EF} = 815844$	$S_{EF} = 4.286$

For the segregation and maximum mixedness models, S_{EF} is much lower than for the CSTR but still far greater than for the PFR. The CSTR and PFR values are unchanged as they do not depend on $E(t)$.

Problem P13-17_B

Multiple parallel reactions, isothermal

Asymmetric RTD : $E = \text{IF } (t \leq 1.26) \text{ THEN } (E_1) \text{ ELSE } (E_2)$

$$E_1 = -2.104t^4 + 4.167t^3 - 1.596t^2 - 0.353t - 0.004$$

$$E_2 = -2.104t^4 + 17.037t^3 - 50.247t^2 + 62.964t - 27.402$$

$$k_{D1} = 0.25 \text{ dm}^6/\text{mol}^2 \cdot \text{min}, \quad k_{E2} = 0.1 \text{ dm}^3/\text{mol} \cdot \text{min}, \quad k_{F3} = 5.0 \text{ dm}^6/\text{mol}^2 \cdot \text{min}$$

Part (a)

Segregated model

$$\frac{dC_A}{dt} = -k_{D1} C_A C_B^2 - 3k_{E2} C_A C_D$$

$$\frac{dC_B}{dt} = -2k_{D1} C_A C_B^2 - k_{F3} C_B C_C^2$$

$$\frac{dC_C}{dt} = k_{D1} C_A C_B^2 + k_{E2} C_A C_D - 2k_{F3} C_B C_C^2$$

$$\frac{dC_D}{dt} = k_{D1} C_A C_B^2 - 2k_{E2} C_A C_D + k_{F3} C_B C_C^2$$

$$\frac{dC_E}{dt} = k_{E2} C_A C_D$$

$$\frac{dC_F}{dt} = k_{F3} C_B C_C^2$$

$$\frac{d\bar{C}_A}{dt} = C_A E(t)$$

$$\frac{d\bar{C}_C}{dt} = C_C E(t)$$

$$\frac{d\bar{C}_E}{dt} = C_E E(t)$$

$$\frac{d\bar{C}_B}{dt} = C_B E(t)$$

$$\frac{d\bar{C}_D}{dt} = C_D E(t)$$

$$\frac{d\bar{C}_F}{dt} = C_F E(t)$$

$$S_{CD} = \frac{\bar{C}_C}{\bar{C}_D}$$

$$S_{DE} = \frac{\bar{C}_D}{\bar{C}_E}$$

$$S_{EF} = \frac{\bar{C}_E}{\bar{C}_F}$$

Problem P13-17

Equations:

	<u>Initial value</u>
$d(Ca)/d(t) = (-kd1 \cdot Ca \cdot (Cb^2)) - (3 \cdot ke2 \cdot Ca \cdot Cd)$	1.5
$d(Cb)/d(t) = -(2 \cdot kd1 \cdot Ca \cdot (Cb^2)) - (kf3 \cdot Cb \cdot (Cc^2))$	2
$d(Cd)/d(t) = (kd1 \cdot Ca \cdot (Cb^2)) - (2 \cdot ke2 \cdot Ca \cdot Cd) + (kf3 \cdot Cb \cdot (Cc^2))$	0
$d(Cc)/d(t) = (kd1 \cdot Ca \cdot (Cb^2)) + (ke2 \cdot Ca \cdot Cd) - (2 \cdot kf3 \cdot Cb \cdot (Cc^2))$	0
$d(Ce)/d(t) = ke2 \cdot Ca \cdot Cd$	0
$d(Cabar)/d(t) = Ca \cdot E$	1e-05
$d(Cf)/d(t) = kf3 \cdot Cb \cdot (Cc^2)$	0
$d(Cbbar)/d(t) = Cb \cdot E$	1e-05
$d(Ccbar)/d(t) = Cc \cdot E$	1e-05
$d(Cdbar)/d(t) = Cd \cdot E$	1e-05
$d(Cebar)/d(t) = Ce \cdot E$	1e-05
$d(Cfbar)/d(t) = Cf \cdot E$	1e-05

kd1=0.25

ke2=0.1

kf3=5

$E2 = (-2.104 \cdot (t^4)) + (17.037 \cdot (t^3)) - (50.247 \cdot (t^2)) + (62.964 \cdot (t)) - 27.402$

$E1 = (-2.104 \cdot (t^4)) + (4.167 \cdot (t^3)) - (1.596 \cdot (t^2)) + (0.353 \cdot (t)) - 0.004$

$Scd = Ccbar/Cdbar$

$Sde = Cdbar/Cebar$

$Sef = Cebar/Cfbar$

$E = \text{if}(t \leq 1.26) \text{ then}(E1) \text{ else}(E2)$

$t_0 = 0, \quad t_f = 2.416$

Problem P13-17

<u>Variable</u>	<u>Initial value</u>	<u>Maximum value</u>	<u>Minimum value</u>	<u>Final value</u>
t	0	2.416	0	2.416
Ca	1.5	1.5	0.579486	0.579486
Cb	2	2	0.511616	0.511616
Cd	0	0.674325	0	0.674325
Cc	0	0.197054	0	0.135425
Ce	0	0.106456	0	0.106456
Cabar	1e-05	0.818879	-2.17501e-05	0.818879
Cf	0	0.286089	0	0.286089
Cbbar	1e-05	0.767019	-3.22628e-05	0.767019
Ccbar	1e-05	0.162801	9.89375e-06	0.162801
Cdbar	1e-05	0.59962	9.89383e-06	0.59962
Cebar	1e-05	0.0529211	9.99996e-06	0.0529211
Cfbar	1e-05	0.198527	9.99999e-06	0.198527
kd1	0.25	0.25	0.25	0.25
ke2	0.1	0.1	0.1	0.1
kf3	5	5	5	5
E2	-27.402	0.95674	-27.402	-3.135e-05
E1	-0.004	0.958623	-21.3885	-21.3885
Scd	1	1	0.271507	0.271507
Sde	1	46.651	0.989386	11.3304
Sef	1	1	0.154929	0.266568
E	-0.004	0.958623	-0.004	-3.135e-05

Exit concentrations :

$$\bar{C}_A = 0.819 \text{ mol / dm}^3$$

$$\bar{C}_B = 0.767$$

$$\bar{C}_C = 0.163$$

$$\bar{C}_D = 0.600$$

$$\bar{C}_E = 0.053$$

$$\bar{C}_F = 0.199$$

Selectivities :

$$S_{CD} = 0.272$$

$$S_{DE} = 11.330$$

$$S_{EF} = 0.267$$

Part (b)*Maximum mixedness model*

As the RTD is asymmetric we can use the same equations for $E(\lambda)$ as we did for $E(t)$, with : $E(\lambda) = \text{IF } (\lambda \leq 1.26) \text{ THEN } (E_1) \text{ ELSE } (E_2)$.

$$\frac{dC_A}{d\lambda} = -\sum r_A + (C_A - C_{A0}) \frac{E(\lambda)}{1 - F(\lambda)}$$

$$\frac{dC_A}{d\lambda} = -(-k_{D1} \cdot C_A \cdot C_B^2 - 3k_{E2} \cdot C_A \cdot C_D) + \left((C_A - C_{A0}) \frac{E(\lambda)}{1 - F(\lambda)} \right)$$

The same applies to the equations for the other species as in Part (a).

Problem P13-17Equations:

$$d(C_A)/d(\tau) = \{ (-k_{D1} \cdot C_A \cdot (C_B^2)) - (3 \cdot k_{E2} \cdot C_A \cdot C_D) \} - \{ (C_A - C_{A0}) \cdot E / (1 - F) \} \quad \text{Initial value } 1.5$$

$$d(C_B)/d(\tau) = \{ -(2 \cdot k_{D1} \cdot C_A \cdot (C_B^2)) - (k_{F3} \cdot C_B \cdot (C_C^2)) \} - \{ (C_B - C_{B0}) \cdot E / (1 - F) \} \quad 2$$

$$d(C_D)/d(\tau) = \{ (k_{D1} \cdot C_A \cdot (C_B^2)) - (2 \cdot k_{E2} \cdot C_A \cdot C_D) + (k_{F3} \cdot C_B \cdot (C_C^2)) \} - \{ (C_D - C_{D0}) \cdot E / (1 - F) \} \quad 0$$

$$d(F)/d(\tau) = -E \quad 0.999$$

$$d(C_C)/d(\tau) = \{ (k_{D1} \cdot C_A \cdot (C_B^2)) + (k_{E2} \cdot C_A \cdot C_D) - (2 \cdot k_{F3} \cdot C_B \cdot (C_C^2)) \} - \{ (C_C - C_{C0}) \cdot E / (1 - F) \} \quad 0$$

$$d(C_E)/d(\tau) = (k_{E2} \cdot C_A \cdot C_D) - \{ (C_E - C_{E0}) \cdot E / (1 - F) \} \quad 0$$

$$d(C_F)/d(\tau) = (k_{F3} \cdot C_B \cdot (C_C^2)) - \{ (C_F - C_{F0}) \cdot E / (1 - F) \} \quad 0$$

$$k_{D1} = 0.25$$

$$k_{E2} = 0.1$$

$$C_{A0} = 1.5$$

$$k_{F3} = 5$$

$$C_{B0} = 2$$

```

Cdo=0
Cco=0
Ceo=0
Cfo=0
Sef=Ce/(Cf+0.00001)
Scd=Cc/(Cd+0.00001)
Sde=Cd/(Ce+0.00001)
lam=2.416-t
E2=(-2.104*(lam^4))+17.037*(lam^3)-(50.247*(lam^2))+162
    .964*(lam))-27.402
E1=(-2.104*(lam^4))+4.167*(lam^3)-(1.596*(lam^2))+0.35
    3*(lam))-0.004
E=if(lam<=1.26)then(E1)else(E2)
t0 = 0,    tf = 2.416

```

Problem P13-17

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	2.416	0	2.416
Ca	1.5	1.5	0.846576	0.846576
Cb	2	2	0.824205	0.824205
Cd	0	0.576213	0	0.576213
P	0.999	0.999	0.00932193	0.00932193
Cc	0	0.169878	0	0.161736
Ce	0	0.0538424	0	0.0538424
Cf	0	0.192001	0	0.192001
kdl	0.25	0.25	0.25	0.25
ke2	0.1	0.1	0.1	0.1
Cao	1.5	1.5	1.5	1.5
kf3	5	5	5	5
Cbo	2	2	2	2
Cdo	0	0	0	0
Cco	0	0	0	0
Ceo	0	0	0	0
Cfo	0	0	0	0
Sef	0	0.70501	0	0.280412
Scd	0	1.00008	0	0.280683
Sde	0	690.225	0	10.6999
lam	2.416	2.416	0	0
E2	-3.135e-05	0.95674	-27.402	-27.402
E1	-21.3885	0.958963	-21.3885	-0.004
E	-3.135e-05	0.958963	-0.004	-0.004

Exit concentrations :

$$C_A = 0.847 \text{ mol / dm}^3$$

$$C_B = 0.824$$

$$C_C = 0.162$$

$$C_D = 0.576$$

$$C_E = 0.054$$

$$C_F = 0.192$$

Selectivities :

$$S_{CD} = 0.281$$

$$S_{DE} = 10.7$$

$$S_{EF} = 0.280$$

Part (c)

Ideal CSTR

$$t_m = \tau \quad \text{and} \quad E(t) = \frac{e^{-t/\tau}}{\tau}$$

$$\frac{dC_A}{dt} = v_0(C_{A0} - C_A) + r_A \quad \text{where} \quad r_A = (-k_{d1} \cdot C_A \cdot C_B^2 - 2k_{f2} \cdot C_A \cdot C_D) \\ v_0 = v$$

and so on for the other species.

Problem P13-17

Equations:

Initial value

$$d(C_A)/dt = (v_0 \cdot (C_{A0} - C_A)) + (-k_{d1} \cdot C_A \cdot (C_B^2) - (3 \cdot k_{f2} \cdot C_A \cdot C_D)) \quad 1.5$$

$$d(C_B)/dt = (v_0 \cdot (C_{B0} - C_B)) + (-2 \cdot k_{d1} \cdot C_A \cdot (C_B^2) - (k_{f3} \cdot C_B \cdot (C_C^2))) \quad 2$$

$$d(C_D)/dt = (v_0 \cdot (C_{D0} - C_D)) + (k_{d1} \cdot C_A \cdot (C_B^2) - (2 \cdot k_{f2} \cdot C_A \cdot C_D) + (k_{f3} \cdot C_B \cdot (C_C^2))) \quad 0$$

$$d(C_C)/dt = (v_0 \cdot (C_{C0} - C_C)) + (k_{d1} \cdot C_A \cdot (C_B^2) + (k_{f2} \cdot C_A \cdot C_D) - (2 \cdot k_{f3} \cdot C_B \cdot (C_C^2))) \quad 0$$

$$d(C_E)/dt = (v_0 \cdot (C_{E0} - C_E)) + (k_{f2} \cdot C_A \cdot C_D) \quad 0$$

$$d(C_F)/dt = (v_0 \cdot (C_{F0} - C_F)) + (k_{f3} \cdot C_B \cdot (C_C^2)) \quad 0$$

$$v_0 = 10$$

$$C_{A0} = 1.5$$

$$k_{d1} = 0.25$$

$$k_{f2} = 0.1$$

$$C_{B0} = 2$$

$$k_{f3} = 5$$

$$C_{D0} = 0$$

$$C_{C0} = 0$$

$$C_{E0} = 0$$

$$C_{F0} = 0$$

$$\tau = 5$$

$$Sef = Ce / (Cf + 0.00001)$$

$$Sed = Cc / (Cd + 0.00001)$$

$$Sde = Cd / (Ce + 0.00001)$$

$$E = \exp(-t/\tau) / \tau$$

$$t_0 = 0, \quad t_f = 1$$

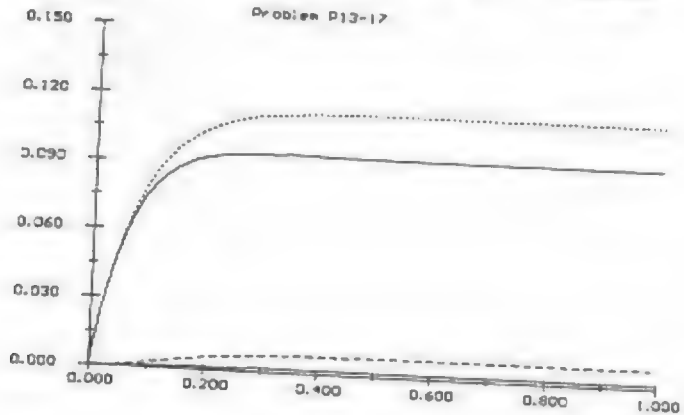
Problem P13-17

Variable	Initial value	Maximum value	Minimum value	Final value
t	0	1	0	1
Ca	1.5	1.5	1.38621	1.38621
Cb	2	2	1.77393	1.77393
Cd	0	0.113856	0	0.113856
Cc	0	0.0949571	0	0.0947184
Ce	0	0.00157803	0	0.00157803
Cf	0	0.00795718	0	0.00795718
vo	10	10	10	10
Ca0	1.5	1.5	1.5	1.5
kd1	0.25	0.25	0.25	0.25
ke2	0.1	0.1	0.1	0.1
Cbo	2	2	2	2
kf3	5	5	5	5
Cdo	0	0	0	0
Cco	0	0	0	0
Ceo	0	0	0	0
Cfo	0	0	0	0
tau	5	5	5	5
Sef	0	0.728226	0	0.198067
Sed	0	1.00009	0	0.831842
Sde	0	682.717	0	71.6961
g	0.2	0.2	0.163746	0.163746

Problem P13-17

KEY:

- Cc
- Cd
- Ce
- Cf



Exit concentrations :

$$C_A = 1.386 \text{ mol} / \text{dm}^3$$

$$C_B = 1.774$$

$$C_C = 0.095$$

$$C_D = 0.114$$

$$C_E = 0.002$$

$$C_F = 0.008$$

$$S_{CD} = 0.832$$

$$S_{DE} = 71.100$$

$$S_{EF} = 0.198$$

Ideal PFR

$t_m = \tau$ and RTD function $E(t) = \delta(t - \tau)$

$$\frac{dC_A}{dV} = \frac{r_A}{v}$$

where

$$r_A = (-k_{D1} \cdot C_A \cdot C_B^2 - 2k_{E2} \cdot C_A \cdot C_D)$$

$$v_0 = v$$

and so on for the other species.

Problem P13-17

Equations:

	Initial value
$d(C_A)/d(V) = \{(-k_{D1} \cdot C_A \cdot (C_B^2)) - (3 \cdot k_{E2} \cdot C_A \cdot C_D)\} / v_0$	1.5
$d(C_B)/d(V) = \{- (2 \cdot k_{D1} \cdot C_A \cdot (C_B^2)) - (k_{F3} \cdot C_B \cdot (C_C^2))\} / v_0$	2
$d(C_D)/d(V) = \{(k_{D1} \cdot C_A \cdot (C_B^2)) - (2 \cdot k_{E2} \cdot C_A \cdot C_D) + (k_{F3} \cdot C_B \cdot (C_C^2))\} / v_0$	0
$d(C_C)/d(V) = \{(k_{D1} \cdot C_A \cdot (C_B^2)) + (k_{E2} \cdot C_A \cdot C_D) - (2 \cdot k_{F3} \cdot C_B \cdot (C_C^2))\} / v_0$	0
$d(C_E)/d(V) = (k_{E2} \cdot C_A \cdot C_D) / v_0$	0
$d(C_F)/d(V) = (k_{F3} \cdot C_B \cdot (C_C^2)) / v_0$	0

$$k_F = 5$$

$$k_{D1} = 0.25$$

$$k_{E2} = 0.1$$

$$v_0 = 10$$

$$S_{ef} = C_e / (C_f + 0.00001)$$

$$S_{ed} = C_e / (C_d + 0.00001)$$

$$S_{de} = C_d / (C_e + 0.00001)$$

$$V_0 = 0, \quad V_f = 50$$

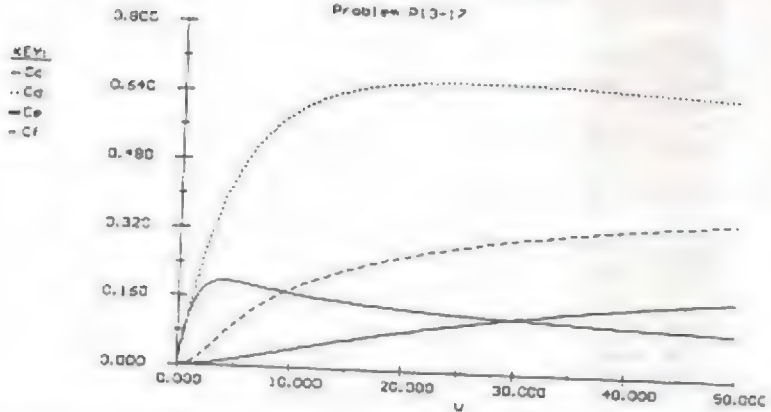
Problem P13-17

Variable	Initial value	Maximum value	Minimum value	Final value
V	0	50	0	50
Ca	1.5	1.5	0.310006	0.310006
Cb	2	2	0.338482	0.338482
Cd	0	0.67513	0	0.651626
Cc	0	0.297055	0	0.105508
Ce	0	0.180102	0	0.180102
Cf	0	0.362141	0	0.362141
kf3	5	5	5	5
kd1	0.25	0.25	0.25	0.25
ke2	0.1	0.1	0.1	0.1
vo	10	10	10	10
Sef	0	0.71031	0	0.497311
Sed	0	1.00004	0	0.161912
Sde	0	695.865	0	3.6179

13-60

P13-17 cont'd

Problem P13-17



Exit concentrations :

$$C_A = 0.310 \text{ mol / dm}^3$$

$$C_B = 0.338$$

$$C_C = 0.106$$

$$C_D = 0.652$$

$$C_E = 0.180$$

$$C_F = 0.362$$

Selectivities :

$$S_{CD} = 0.162$$

$$S_{DE} = 3.618$$

$$S_{EF} = 0.497$$

Segregated

$$S_{CD} = 0.272$$

$$S_{DE} = 11.330$$

$$S_{EF} = 0.267$$

Maximum M

$$S_{CD} = 0.281$$

$$S_{DE} = 10.7$$

$$S_{EF} = 0.280$$

CSTR

$$S_{CD} = 0.832$$

$$S_{DE} = 71.100$$

$$S_{EF} = 0.198$$

PFR

$$S_{CD} = 0.162$$

$$S_{DE} = 3.618$$

$$S_{EF} = 0.497$$

S_{CD} is significantly greater than for the others, because exit C_D is lower.

Similarly S_{DE} is much greater in the CSTR than for the others, because exit C_E is so low. This is because the achievable conversion in a CSTR is not so high.

No solution will be given.

Problem P14-2_s

Part (a)

The correlations between Re and Da show what flow conditions (characterised by Re) gives the greatest or smallest Da and hence dispersion. To minimise dispersion an Re of $\sim 10 - 20$ or $Re > 10^5$ gives the lowest value for Da . $Re = \frac{\rho \cdot u \cdot d}{\mu}$ the design of the

vessel could be altered (diameter) for a given fluid and flowrate. To maximise dispersion, either a very low Re (< 0.1) or $Re \sim 2300$ will give the maximum Da values.

For a packed bed, the dispersion also depends on the Schmidt number as well as the Re .

Part (b)

May be a good approximation if C_A does not change very much with time, i.e. A is in excess, in which case C_{AO} should not be divided by anything.

Linearizing the non 1st order reactions may give significantly inaccurate results using eqn 14-40, which can be tested experimentally by recording tracer concentrations with time and using the tanks in series model for a conversion comparison.

Part (c)

Verify when both models are equivalent, i.e. when the relation $Bo = 2(n-1)$ is valid, should give similar results.

Part (d)

Closed vessel dispersion model :

q is probably the most important term :

$$q = \sqrt{1 + \frac{4Da}{Pe_r}} = \sqrt{1 + \frac{4kDa}{UL}}$$

so the most important group of parameters is $\frac{k}{UL}$ wrt conversion.

For the ideal plug flow, tank in series and ideal CSTR models, k is the parameter to which conversion is most sensitive.

Part (e)

$$V = \text{constant} = \pi \cdot R^2 L = 3.14 \cdot 5^2 \cdot 636 = 49951 \text{ cm}^3$$

$$\text{gives } L = \frac{49951}{\pi \cdot R^2}$$

Figure 14-5 from the text book 3rd edn :

$$\text{Re} \cdot \text{Sc} = \frac{u \cdot D_i}{D_{AB}}$$

for values of $\text{Re} \cdot \text{Sc} > 10$:

$$\text{Fig 14-5 gives dispersion coefficient } D_a = \frac{u^2 D_i^2}{192 \cdot D_{AB}}$$

$$\text{Pe} = \frac{U \cdot L}{D_a}$$

$$\text{1st order reaction : Damkohler no. } Da = \tau k = 5.15 \cdot 0.25 = 1.288$$

$$X = 1 - \frac{4q \exp\left(\frac{\text{Pe}_r}{2}\right)}{\left[(1+q)^2 \exp\left(\frac{\text{Pe}_r q}{2}\right)\right] - \left[(1-q)^2 \exp\left(-\frac{\text{Pe}_r q}{2}\right)\right]}$$

$$\text{where } q = \sqrt{1 + \frac{4Da}{\text{Pe}_r}}$$

P14-2 cont'd

Using Excel spreadsheet :

V (cm ³)	U (cm/s)						
49951.28	0.01						
D _i (cm)	L(cm)	(Re)(Sc)	D _a (cm ² /s)	Pe	Da	q	x
1	63600	1000	0.05	5.21	1.288	1.410	0.666
5	2544	5000	1.30	26.04	1.288	1.094	0.708
10	636	10000	5.21	52.08	1.288	1.048	0.716
20	159	20000	20.83	104.17	1.288	1.024	0.720
30	70.67	30000	46.88	156.25	1.288	1.016	0.721
40	39.75	40000	83.33	208.33	1.288	1.012	0.722
50	25.44	50000	130.21	260.42	1.288	1.010	0.722
60	17.67	60000	187.50	312.50	1.288	1.008	0.723
70	12.98	70000	255.21	364.58	1.288	1.007	0.723
80	9.94	80000	333.33	416.67	1.288	1.006	0.723
90	7.85	90000	421.88	468.75	1.288	1.005	0.723
100	6.36	100000	520.83	520.83	1.288	1.005	0.723

A velocity of 0.1 cm/s gives very large Pe values > 1000, and hence conversion cannot be calculated.

However a velocity of 0.01 cm/s gives a full range of results for 1 to 100 cm tube diameters.

It is clear that conversion increases with diameter, because the dispersion increases, better mixing. There is no diameter which provides a maximum or minimum conversion in this range except at the extreme values of 1 cm to 100 cm.

Part (f)

Open vessel : $\frac{\sigma^2}{t_m^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2}$

from data : $\tau = \int_0^{\infty} tE(t)dt = 5.15 \text{ min}$

$$\sigma^2 = \int_0^{\infty} (t - \tau)^2 E(t)dt = \int_0^{\infty} t^2 E(t)dt - \tau^2 = 32.63 - 5.15^2 = 6.10 \text{ min}^2$$

14-3

P14-2 cont'd

but

$$t_m = \left(1 + \frac{2}{Pe_r}\right) \tau$$

$$\frac{\sigma^2}{\left(1 + \frac{2}{Pe_r}\right)^2 \tau^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2}$$

Iterating gives $Pe_r = 5$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}}$$

$$Da = \tau k = 5.15 * 0.25 = 1.2875$$

$$q = 1.425$$

$$X = 1 - \frac{4q \exp(Pe_r/2)}{\left[(1+q)^2 \exp(Pe_r q/2)\right] - \left[(1-q)^2 \exp(-Pe_r q/2)\right]}$$

$$= 1 - \frac{4 * 1.425 * \exp(5/2)}{\left[(1+1.425)^2 \exp(5 * 1.425/2)\right] - \left[(1-1.425)^2 \exp(-5 * 1.425/2)\right]}$$

$$= 0.665$$

Closed model : $X = 68 \%$

Open model : $X = 67 \%$

Part (g)

$$\alpha = 0.75 \quad \beta = 0.15$$

$$V_s + V_d = V = 1.0 \text{ m}^3$$

$$v_o = v_s + v_b = 0.1 \text{ m}^3/\text{min}$$

14-4

P14-2 cont'd

$$\alpha = \frac{V_s}{V} = 0.75$$

$$\beta = \frac{v_b}{v_o} = 0.15$$

$$V_s = \alpha V = 0.75 * 1 = 0.75 \text{ m}^3$$

$$v_s = v_o - v_b = v_o - v_o \beta = 0.1 - (0.1 * 0.15) = 1 - 0.015 = 0.085 \text{ m}^3/\text{min}$$

$$\tau = \frac{V_s}{v_s} = \frac{0.75}{0.085} = 8.82 \text{ min}$$

$$k = 0.28 \text{ m}^3/\text{kmol} \cdot \text{min}, \quad C_{A0} = 2 \text{ kmol/m}^3$$

$$C_{As} = \frac{\sqrt{1 + 4\tau k C_{A0}} - 1}{2\tau k} = 0.72 \text{ kmol/m}^3$$

$$C_A = \frac{v_o - v_s}{v_o} C_{A0} + \frac{v_s}{v_o} C_{As} = \frac{0.1 - 0.085}{0.1} * 2 - \frac{0.085}{0.1} * 0.72 = 0.912$$

$$X = 1 - \frac{0.912}{2.0} = 0.54 \text{ cf } 0.51 \text{ as before.}$$

Part (h)

The model in Fig 14-14a, assumes a "faster" (channelling) reactor and a "slower" uniform reactor. There is a exit age distribution for the faster reactor which occurs as a distinct pulse clearly before the exit age distribution of the second reactor. The fraction of effluent which has been in the real reactor for less than time t , shows a step up from zero when flow leaves from the "faster" reactor. This fraction is the fraction of flow in the "slower" reactor. When the flow leaves the "slower" reactor this fraction becomes one.

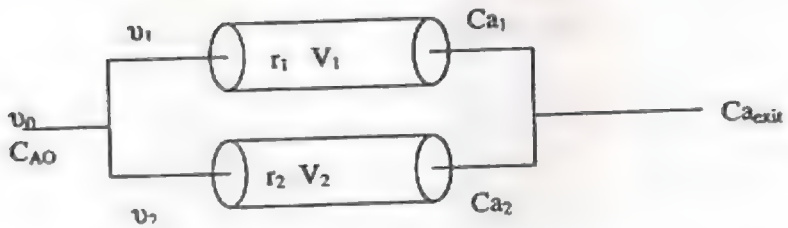
The model in Fig 14-14b is PFR and CSTR in parallel. The exit age distribution for the CSTR is a negative gradient curve, interrupted by the distinct exit age distribution pulse of the PFR. The CSTR will always provide a fraction of effluent which has been inside the reactor for less than time t , which increases with time. But when the effluent exits the PFR at a specified time after zero, this increased effluent is superimposed upon $F(t)$ of the CSTR, giving a combined $F(t)$.

$$\theta_1 = \frac{\alpha}{\beta} = 0.5$$

$$\theta_2 = \frac{1 - \alpha}{1 - \beta} = 1.5$$

14-5

P14-2 cont'd



$$\alpha = \frac{V_1}{V}$$

$$\beta = \frac{v_1}{v}$$

$$\tau = \frac{V}{v} = 5 \text{ min}$$

PFR mol balance : $\frac{dX}{dV} = -\frac{r_A}{F_{A0}}$

rate law : $-r_A = k \cdot C_A^2$

Stoichiometry : liquid phase $C_A = C_{A0} (1 - X)$

2nd order PFR : $\frac{V}{v} = \frac{1}{k \cdot C_{A0}^2} \left[2\varepsilon(1 + \varepsilon) \ln(1 - X) + \varepsilon^2 X + \frac{(1 + \varepsilon^2)X}{1 - X} \right]$

$$\varepsilon = y_{A0} \cdot \delta \quad \delta = \frac{c}{a} + \frac{b}{a} - 1 = \frac{1}{2} + \frac{1}{2} - 1 = 0$$

$$\varepsilon = 0$$

Determining α and β :

$$\frac{\alpha}{\beta} = \frac{V_1 v_0}{V v_1} = 0.5 \quad \rightarrow \quad V_1 = 2.5 v_1$$

$$1 - \frac{V_1}{V} = 1.5 \left(1 - \frac{v_1}{v} \right)$$

$$1 - 2.5 \frac{v_1}{V} = 1.5 - 1.5 \frac{v_1}{v}$$

$$V - 2.5 v_1 = 1.5 V - 7.5 v_1$$

$$0.5 V = 5 v_1$$

$$V = 10 v_1$$

14-6

P14-2 cont'd

gives

$$\alpha = \frac{2.5v_1}{10v_1} = 0.25$$

$$\beta = \frac{V_1/2.5}{V/5} = \frac{5\alpha}{2.5} = 0.5$$

Now

$$\tau = \frac{\tau_1 + \tau_2}{2} = \frac{V_1/v_1 + V_2/v_2}{2} = 5 \text{ min}$$

hence

$$V_1/v_1 + V_2/v_2 = 10$$

but

$$V_1 = 2.5 v_1 \rightarrow V_2 = 7.5 v_2$$

gives

$$\tau_1 = 2.5 \text{ min} \quad \tau_2 = 7.5 \text{ min}$$

substituting into

$$\frac{V}{v} = \frac{1}{k \cdot C_{A0}^2} \left[2\epsilon(1+\epsilon)\ln(1-X) + \epsilon^2 X + \frac{(1+\epsilon^2)X}{1-X} \right]$$

Reactor 1 :

$$2.5 = \frac{1}{0.1 * 2^2} \left[\frac{X_1}{1-X_1} \right]$$

$$1 = \left[\frac{X_1}{1-X_1} \right] \rightarrow X_1 = 0.5$$

$$C_{A1} = C_{A0}(1 - X_1) = 2(1 - 0.5) = 1 \text{ mol/dm}^3$$

Reactor 2 :

$$7.5 = \frac{1}{0.1 * 2^2} \left[\frac{X_2}{1-X_2} \right]$$

$$3 = \left[\frac{X_2}{1-X_2} \right] \rightarrow X_2 = 0.75$$

$$C_{A2} = C_{A0}(1 - X_2) = 2(1 - 0.75) = 0.5 \text{ mol/dm}^3$$

$$C_{A_{out}} = \frac{C_{A1} + C_{A2}}{2} = \frac{1 + 0.5}{2} = 0.75 \text{ mol / dm}^3$$

$$X = \frac{C_{A0} - C_A}{C_{A0}} = \frac{2 - 0.75}{2} = 0.625$$

14-7

Problem P14-3_B

Using the tank in series model :

second order reaction

$$X = \frac{2Da + 1 - \sqrt{4Da + 1}}{2Da}$$

where $Da = k\tau C_{A0}$

$$C_A = C_{A0}(1 - X) \quad X = \frac{C_{A0} - C_A}{C_{A0}}$$

Assume that $\tau = \tau_i$ and that in reactors modelled as more than one tank, that $\tau = \frac{V}{n}$

Number of tanks $n = \frac{\tau^2}{\sigma^2}$ rounded to the nearest integer

Reactor	σ (min)	τ (min)	n	X
Maze & blue	2	2	1	0.50
Green & white	4	4	1	0.61
Scarlet & grey	3.05	4	2	0.69
Orange & blue	2.31	4	3	0.72
Purple & white	5.17	4	1	0.61
Silver & black	2.5	4	3	0.72
Crimson & white	2.5	2	1	0.5

where

Scarlet & grey : $X_1 = 0.5, C_{A1} = 0.5 \rightarrow X_2 = 0.38, C_{A2} = 0.31 \rightarrow X = 0.69$

Orange & blue : $X_1 = 0.43, C_{A1} = 0.57 \rightarrow X_2 = 0.34, C_{A2} = 0.38 \rightarrow X_3 = 0.27,$
 $C_{A3} = 0.28 \rightarrow X = 0.72$

Using the combination of maze & blue followed by crimson & white reactor (same overall conversion either way)

$X_1 = 0.5, C_{A1} = 0.5 \rightarrow X_2 = 0.17, C_{A2} = 0.41 \rightarrow X = 0.59$

The orange & blue or silver & black reactors which both approximate to 3 tanks in series give the greatest conversion.

Part (b)

Try :

Green & white and Maze & blue : $X_1 = 0.61, C_{A1} = 0.39 \rightarrow X_2 = 0.34, C_{A2} = 0.26 \rightarrow$
 $X = 0.74$

P14-3 cont'd

Scarlet & grey and Maze & blue : $X_1 = 0.69$, $C_{A1} = 0.31 \rightarrow X_2 = 0.42$, $C_{A2} = 0.18 \rightarrow X = 0.82$

Orange & blue and Maze & blue : $X_1 = 0.72$, $C_{A1} = 0.28 \rightarrow X_2 = 0.40$, $C_{A2} = 0.17 \rightarrow X = 0.83$

The highest conversion is now obtained from the Orange & blue reactor combined with the Maze & blue reactor.

Problem 14-4_n

1st order, $k_1 = 0.0167 \text{ /s}$, $\epsilon = 0.5$, $d_p = 0.1 \text{ cm}$,

$$v = \frac{\mu}{\rho} = 0.01 \text{ cm}^2 / \text{s} \quad L = 10 \text{ cm}, \quad U = 1 \text{ cm/s}$$

$$\text{Re} = \frac{\rho U d_p}{\mu} = \frac{1 * 0.1}{0.01} = 10 \quad \text{Sc} = \frac{\nu}{D_{AB}} \quad \text{no data concerning } D_{AB}$$

From packed bed correlation for D_s , and liquid phase region of graph,

$$\text{gives } \frac{D_s \epsilon}{U d_p} = 2 \text{ approx.} \quad \rightarrow \quad D_s = \frac{2 U d_p}{\epsilon} = \frac{2 * 1 * 0.1}{0.5} = 0.4 \text{ cm}^2 / \text{s}$$

$$\text{Pe}_r = \frac{UL}{D_s} = \frac{1 * 10}{0.4} = 25$$

$$X = 1 - \frac{4q \exp\left(\frac{\text{Pe}_r}{2}\right)}{\left[(1+q)^2 \exp\left(\frac{\text{Pe}_r q}{2}\right)\right] - \left[(1-q)^2 \exp\left(-\frac{\text{Pe}_r q}{2}\right)\right]}$$

$$q = \sqrt{1 + \frac{4Da}{\text{Pe}_r}}$$

$$\text{Da} = \tau k \quad \text{and} \quad \tau = \frac{L}{U} = \frac{10}{1} = 10 \text{ s} \quad \rightarrow \quad \text{Da} = 10 * 0.0167 = 0.167$$

$$\rightarrow \quad q = 1.013$$

14-9

P14-4 cont'd

$$X = 1 - \frac{4 * 1.013 * \exp\left(\frac{25}{2}\right)}{\left[(1 + 1.013)^2 \exp\left(\frac{25 * 1.013}{2}\right)\right] - \left[(1 - 1.013)^2 \exp\left(\frac{-25 * 1.013}{2}\right)\right]} = 0.15$$

Conversion $X = 15 \%$

Problem P14-5A

Part (a)

Assuming the Peclet-Bodenstein relation : $n = \frac{Bo}{2} + 1$

$$\text{where } Bo = \frac{UL}{D_s}$$

To estimate Bo, $Re = \frac{du}{\nu} = \frac{5 * 2}{0.01} = 1000$

$$Sc = \frac{\nu}{D_{AB}} = \frac{0.01}{0.005} = 2$$

From gas phase dispersion correlation chart, $\frac{D_s}{u.d} = 8$

gives $D_s = 8 * 2 * 5 = 80 \text{ cm}^2/\text{s}$

$$Bo = \frac{2 * 200}{80} = 5$$

$$n = \frac{5}{2} + 1 = 3.5$$

Part (b)

Using individual reactor material balances :

Reactor 1 :

mol balance : $X = -\frac{r_A V}{F_{A0}}$

14-10

P14-5 cont'd

rate law :

$$-r_A = k.C_A^2$$

stoichiometry :
change

$$C_A = C_{A0} (1 - X_1) \quad \delta = 0 \text{ and } \epsilon = 0 \text{ hence no volume}$$

$$X_1 = \frac{k.C_{A0}^2(1-X_1)^2}{v.C_{A0}} = \frac{25 \cdot 0.01}{0.039}(1-X_1)^2$$

$$X_1 = 6.366 (1 - X_1)^2 \rightarrow 0.674$$

$$C_{A1} = C_{A0} (1 - X_1) = 0.00326 \text{ mol/dm}^3$$

Reactor 2 :

$$X_2 = \frac{k.C_{A1}(1-X_2)^2}{v} \rightarrow \frac{X_2}{(1-X_2)^2} = \frac{25 \cdot 0.00326}{0.039} = 2.0897$$

$$X_2 = 0.507$$

$$C_{A2} = C_{A1} (1 - X_2) = 0.00326 (1 - 0.507) = 0.001607 \text{ mol/dm}^3$$

Reactor 3 :

$$X_3 = \frac{k.C_{A2}(1-X_3)^2}{v} \rightarrow \frac{X_3}{(1-X_3)^2} = \frac{25 \cdot 0.001607}{0.039} = 1.0302$$

$$X_3 = 0.387$$

$$C_{A3} = C_{A2} (1 - X_3) = 0.001607 (1 - 0.387) = 0.000985 \text{ mol/dm}^3$$

Reactor 4 :

$$X_4 = \frac{k.C_{A3}(1-X_4)^2}{v} \rightarrow \frac{X_4}{(1-X_4)^2} = \frac{25 \cdot 0.000985}{0.039} = 0.6315$$

$$X_4 = 0.305$$

$$C_{A4} = C_{A3} (1 - X_4) = 0.000985 (1 - 0.305) = 0.000685 \text{ mol/dm}^3$$

Bounds on conversion

3 tanks

$$X = \frac{C_{A0} - C_{A3}}{C_{A0}} = 0.9015$$

4 tanks

$$X = \frac{C_{A0} - C_{A4}}{C_{A0}} = 0.9315$$

Part (c)

Let $U = 0.1 \text{ cm/s}$

$$Re = 50$$

$$Sc = 2$$

14-11

P14-5 cont'd

From gas phase dispersion correlation chart, $\frac{D_a}{u \cdot d_i} = 0.5$

gives $D_a = 0.5 \cdot 0.1 \cdot 5 = 0.25 \text{ cm}^2/\text{s}$

$$Bo = \frac{0.1 \cdot 200}{0.25} = 80$$

$$n = \frac{80}{2} + 1 = 41 \quad \text{probably giving a conversion} \sim 99.99 \%$$

Let $U = 100 \text{ cm/s}$

$$Re = 50000 \quad Sc = 2$$

From gas phase dispersion correlation chart, $\frac{D_a}{u \cdot d_i} = 0.21$

gives $D_a = 0.21 \cdot 100 \cdot 5 = 105 \text{ cm}^2/\text{s}$

$$Bo = \frac{100 \cdot 200}{105} = 190.5$$

$$n = \frac{190.5}{2} + 1 = 96 \quad \text{probably giving a conversion} \sim 99.99 \%$$

Part (d)

$$Re = \frac{d_p u}{\nu} = \frac{0.2 \cdot 4}{0.01} = 80$$

From packed bed dispersion correlation chart, $\frac{D_a \varepsilon}{u \cdot d_p} = 0.55$

$$D_a = \frac{0.55 \cdot 4 \cdot 0.2}{0.4} = 1.1$$

$$Bo = \frac{4 \cdot 200}{1.1} = 727$$

$$n = \frac{727}{2} + 1 = 364.5 \quad \text{probably giving a conversion} \sim 99.99 \%$$

14-12

P14-5 cont'd

Part (e)

$$\text{Part (a)} \quad \text{Re} = \frac{d_{iu} \rho}{\mu} = \frac{5 * 4 * 0.001}{0.1} = 0.2$$

$$\text{Sc} = \frac{\nu}{D_{AB}} = \frac{100}{5e-6} = 2 * 10^7$$

This is off the scale of the graph for liquid phase dispersion, hence D_A cannot be evaluated.

Problem P14-6A

a) Closed:

$$\frac{\sigma^2}{tm^2} = \frac{2}{Pe_r} = \frac{2}{Pe_r^2} (1 - e^{-Pe_r})$$
$$= 7.54$$

Open:

$$\frac{\sigma^2}{tm^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2} = 11.68$$

b)

$$\tau = \frac{tm}{1 + 2/Pe_r} = 4.40$$

$$V_s = \tau * v_0 = 263.8 dm^3$$

$$V_D = V - V_s = 156.2 dm^3$$

$$\% \text{ dead volume} = \frac{156.2}{420} = 37.2\%$$

14-13

P14-6 cont'd

c)

$$X = 1 - \frac{4q \exp(Pe_r/2)}{(1+q)^2 \exp(Pe_r q/2) - (1-q)^2 \exp(-Pe_r q/2)} = 0.570 \text{ dispersion}$$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}} = 1221$$

$$Da = k\tau = 0.927$$

$$n = \frac{\tau^2}{\sigma^2} = 4.35$$

$$x = 1 - \frac{1}{(1 + \tau_r K)^n} = 0.568, \text{ tanks in series}$$

$$\text{PFR : } X = 1 - e^{-x}$$

$$\text{CSTR : } X = 0.481$$

Part (d)

Tanks in series model : $n = \frac{\tau^2}{\sigma^2} = \frac{4.43^2}{2.4^2} = 3.407$

1st order reaction, so n can be a non-integer : $X = 1 - \frac{1}{(1 + \tau k)^n}$

14-14

P14-6 cont'd

$$X = 1 - \frac{1}{\left(1 + \frac{\tau}{n} k\right)^n} = 1 - \frac{1}{\left(1 + \frac{4.43}{3.407} 0.18\right)^{3.407}} = 0.51$$

PFR : $X = 1 - e^{-k\tau} = 1 - e^{-Da} = 1 - e^{-0.797} = 0.55$

CSTR : $X = \frac{k\tau}{1 + k\tau} = \frac{0.797}{1 + 0.797} = 0.44$

	X
Dispersion	53 %
Tank in series	51 %
PFR	55 %
CSTR	44 %

Problem P14-7A

1st order, irreversible, pulse tracer test $\rightarrow \sigma^2 = 65 \text{ s}^2$ and $t_m = 10 \text{ s}$

For a 1st order reaction, PFR : $X = 1 - e^{-k\tau} = 0.98$

Need τ and k . There being no data for diffusivity (Schmidt number) Da and hence Pe_r cannot be obtained using tubular flow correlations.

Therefore assume closed vessel dispersion model :

$$t_m = \tau = 10 \text{ s}$$

$$k = -\frac{\ln(1-X)}{\tau} = -\frac{\ln(1-0.98)}{10} = 0.39 \text{ s}^{-1}$$

$$\frac{\sigma^2}{t_m^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2} (1 - e^{-Pe_r}) = \frac{65}{10^2} = 0.65$$

14-15

P14-7 cont'd

iterating $\rightarrow Pe_r = 1.5$

$$X = 1 - \frac{4q \exp(Pe_r/2)}{\left[(1+q)^2 \exp(Pe_r q/2)\right] - \left[(1-q)^2 \exp(-Pe_r q/2)\right]}$$

$$Da = \tau k = 10 * 0.39 = 3.9$$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}} = \sqrt{1 + \frac{4 * 3.9}{1.5}} = 3.376$$

$$X = 1 - \frac{4 * 3.376 \exp(1.5/2)}{\left[(1+3.376)^2 \exp(1.5 * 3.376/2)\right] - \left[(1-3.376)^2 \exp(-1.5 * 3.376/2)\right]} = 0.88$$

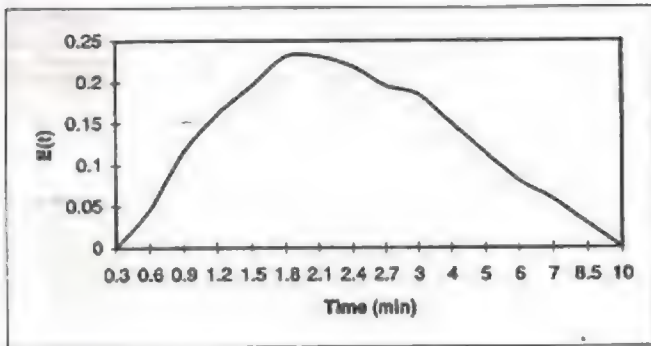
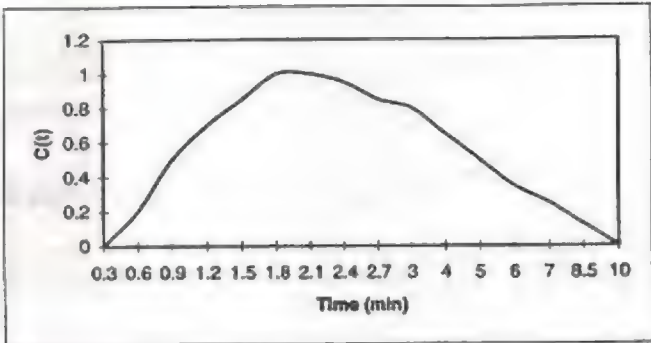
Conversion for the real reactor assuming the closed dispersion model is some what less than for the ideal PFR.

Problem P14-8_a

t (min)	C(t)	E(t)	t.E(t)	(t - t _m) ² .E(t)
0.3	0	0	0.000	0.000
0.6	0.2	0.046	0.028	0.444
0.9	0.5	0.115	0.104	0.907
1.2	0.7	0.161	0.193	1.013
1.5	0.85	0.196	0.294	0.956
1.8	1	0.231	0.416	0.841
2.1	1	0.231	0.485	0.597
2.4	0.95	0.219	0.526	0.375
2.7	0.85	0.196	0.529	0.199
3	0.8	0.185	0.555	0.093
4	0.65	0.15	0.600	0.013
5	0.5	0.115	0.575	0.192
6	0.35	0.081	0.486	0.426
7	0.25	0.058	0.406	0.629
8.5	0.125	0.029	0.247	0.666
10	0	0	0.000	0.000

14-16

P14-8 cont'd



$$E(t) = \frac{C(t)}{\int_0^{\infty} C(t) dt} = \frac{C(t)}{4.335}$$

$$t_m = \int_0^{\infty} t \cdot E(t) \cdot dt = 3.708 \text{ min}$$

Part (b)

Choosing the tanks in series model :

$$\sigma^2 = \int_0^{\infty} (t - t_m)^2 E(t) \cdot dt = 4.144 \text{ min}^2$$

$$n = \frac{t_m^2}{\sigma^2} = \frac{3.708^2}{4.144} = 3.318 \text{ tanks.}$$

14-17

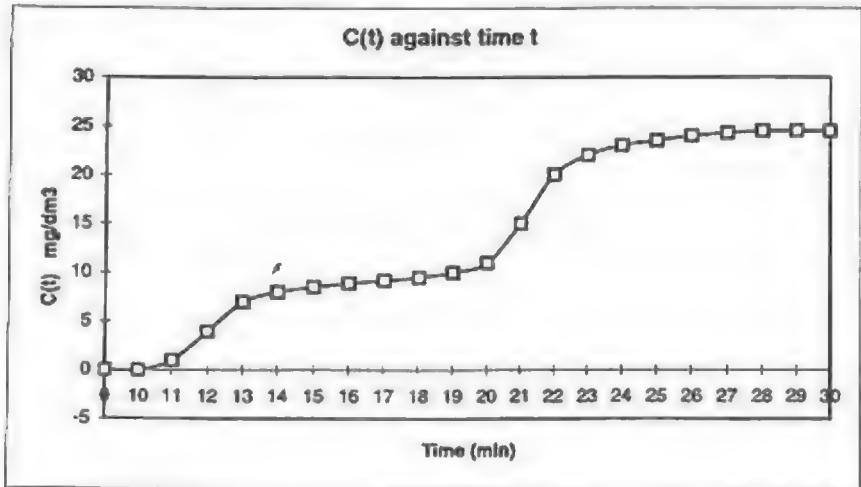
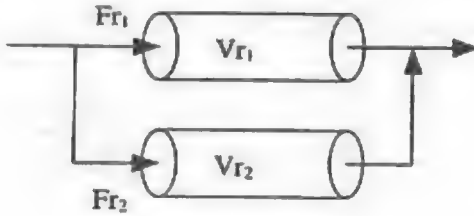
Part (c)

No solution will be given.

Problem P14-9C

Part (a)

Plug flow reactors in parallel.



P14-9 cont'd

time (min)	C(t)	E(t)	X(t)	X(t)E(t)	F(t)	tE(t)	t^2E(t)
0	0	0	0	0.0000	0	0	0
10	0	0	0.5	0.0000	0	0	0
11	1	0.0034	0.52	0.0018		0.0374	0.4114
12	4	0.0138	0.5454	0.0075		0.1656	1.9872
13	7	0.0241	0.5652	0.0136	0.03097	0.3133	4.0729
14	8	0.0276	0.5833	0.0161		0.3864	5.4096
15	8.5	0.0293	0.6	0.0176		0.4395	6.5925
16	8.9	0.0307	0.6154	0.0189	0.1251	0.4912	7.8592
17	9.2	0.0317	0.6296	0.0200		0.5389	9.1613
18	9.5	0.0327	0.6429	0.0210		0.5886	10.5948
19	10	0.0345	0.6552	0.0226	0.2327	0.6555	12.4545
20	11	0.0379	0.6667	0.0253		0.758	15.16
21	15	0.0517	0.6774	0.0350		1.0857	22.7997
22	20	0.0689	0.6875	0.0474	0.3866	1.5158	33.3476
23	22	0.0758	0.697	0.0528		1.7434	40.0982
24	23	0.0793	0.7059	0.0560		1.9032	45.6768
25	23.5	0.081	0.7143	0.0579	0.6434	2.025	50.625
26	24	0.0827	0.7222	0.0597		2.1502	55.9052
27	24.3	0.838	0.7297	0.6115		22.626	610.902
28	24.5	0.0845	0.7368	0.0623	0.9206	2.366	66.248
29	24.5	0.0845	0.7436	0.0628		2.4505	71.0645
30	24.5	0.0845	0.75	0.0634	1	2.535	76.05

$$E(t) = \frac{C(t)}{\int_0^t C(t) dt} = \frac{C(t)}{290.1}$$

$$F(t) = \int_0^t E(t) dt$$

Part (b)

$$\frac{V_{r1}}{V_{total}} = \frac{v \int_0^{20} C(t) dt}{v \int_{10}^{30} C(t) dt} = \frac{71.5}{290.1} = 0.25$$

$$V_{r1} = 0.25 V_{total}$$

$$\frac{F_{r1}}{F_{total}} = \frac{v C_{r1}}{v C_{total}} = \frac{9.0}{24.5} = 0.37$$

$$F_{r1} = 0.37 F_{total}$$

14.19

P14-9 cont'd

Part (c)

$$\text{PFR : } \frac{dC_A}{dt} = -k \cdot C_A^2$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

$$\frac{1}{C_{A0}} \left(\frac{1}{1-X} - 1 \right) = kt$$

$$X = 1 - \frac{1}{1 + kC_{A0}t} = \frac{kC_{A0}t}{1 + kC_{A0}t}$$

$$X = 1 - \frac{1}{1 + \frac{(0.1 \text{ min})(1 \text{ m}^3)}{(0.06 \text{ m}^3 / \text{min})}} = 0.625$$

Part (d)

$$\text{Segregation model : } \bar{X} = \int_0^{\infty} X(t)E(t)dt$$

$$X(t) = \frac{kC_{A0}t}{1 + kC_{A0}t}$$

$$\bar{X} = 0.69$$

Part (e)

Maximum mixedness model :

Using Euler's method for numerical integration. Start with $\lambda = 30$ min and $X = 0$

λ (min)	X
30	0
28	0.2
25	0.2557
22	0.3357
19	0.4228
16	0.4782
13	0.5242
10	0.5921

14-20

P14-9 cont'd

$$X_{i+1} = X_i + (\Delta\lambda) \left[\frac{X(\lambda_i)}{1 - F(\lambda)} X_i - k \cdot C_{AO}(1 - X_i)^2 \right]$$

$$X = 0.59$$

Part (f)

Dispersion model : $\int_0^{\infty} E(t) dt = 23.1307 \quad \tau = \frac{V}{v} = \frac{1m^3}{0.06m^3/min} = 16.7 \text{ min}$

$$\int_0^{\infty} t^2 E(t) dt = 557.969$$

$$\sigma^2 = 557.969 - (23.1307)^2 = 22.94$$

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r^2} [Pe_r - 1 + e^{-Pe_r}] = \frac{22.94}{16.7^2} = 0.08258$$

$$Pe_r = 23$$

$$Da = k \cdot C_{AO} \cdot \tau = 0.1 \cdot 23.1307 = 2.313$$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}} = \sqrt{1 + \frac{4 \cdot 2.312}{23}} = 1.18$$

$$\frac{Pe_r q}{2} = \frac{23 \cdot 1.18}{2} = 13.6$$

$$X = 1 - \frac{4q \exp(Pe_r/2)}{\left[(1+q)^2 \exp(Pe_r q/2) \right] - \left[(1-q)^2 \exp(-Pe_r q/2) \right]}$$

$$X = 1 - \frac{4 \cdot 1.18 \cdot \exp(23/2)}{\left[(1+1.18)^2 \exp(13.6) \right] - \left[(1-1.18)^2 \exp(-13.6) \right]}$$

$$X = 0.88$$

Summary :

	Conversion
PFR with bypass	0.63
Segregation	0.69
Maximum mixedness	0.59
Dispersion	0.88

14-21

Problem P14-11a

Given :

2nd order irreversible reaction, isothermal,

mol/dm³

$V = 1000 \text{ dm}^3$ $v_0 = 1 \text{ dm}^3/\text{s}$ $k = 0.005 \text{ dm}^3/\text{mol.s}$ $C_{A0} = 10$

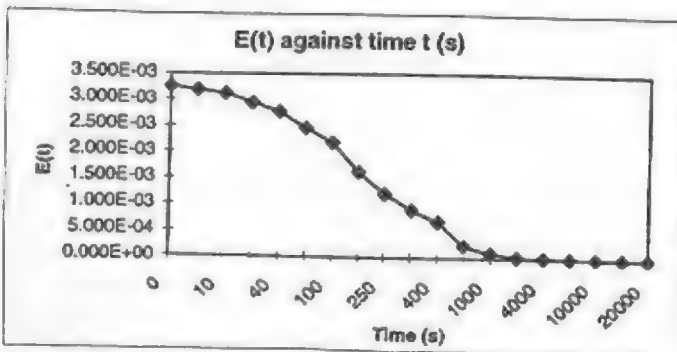
Part (a)

(1) Maximum segregation :

$$X = \frac{kC_{A0}t}{1 + kC_{A0}t} = \frac{0.005 * 10 * t}{1 + (0.005 * 10 * t)}$$

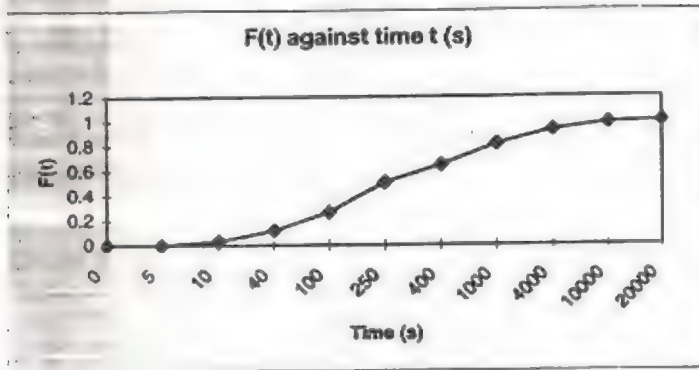
$$\bar{X} = \int_0^\infty X(t)E(t)dt = 0.868$$

t	E(t) (/s)	X(t)	X(t)E(t)	F(t)	tE(t)	t ² E(t)
0	3.250E-03	0.000	0.00E+00		0.000E+00	0.00
5	3.187E-03	0.200	6.37E-04		1.594E-02	0.08
10	3.124E-03	0.333	1.04E-03	0.032	3.124E-02	0.31
25	2.945E-03	0.556	1.64E-03		7.363E-02	1.84
40	2.776E-03	0.667	1.85E-03	0.118	1.110E-01	4.44
70	2.468E-03	0.778	1.92E-03		1.728E-01	12.09
100	2.194E-03	0.833	1.83E-03	0.265	2.194E-01	21.94
175	1.637E-03	0.897	1.47E-03		2.865E-01	50.13
250	1.224E-03	0.926	1.13E-03	0.51	3.060E-01	76.50
325	9.184E-04	0.942	8.65E-04		2.985E-01	97.01
400	6.913E-04	0.952	6.58E-04	0.648	2.765E-01	110.61
700	2.366E-04	0.972	2.30E-04		1.656E-01	115.93
1000	9.755E-05	0.980	9.56E-05	0.818	9.755E-02	97.55
2500	2.691E-05	0.992	2.67E-05		6.728E-02	168.19
4000	1.839E-05	0.995	1.83E-05	0.928	7.356E-02	294.24
7000	8.689E-06	0.997	8.66E-06		6.082E-02	425.76
10000	4.104E-06	0.998	4.10E-06	0.984	4.104E-02	410.40
15000	1.176E-06	0.999	1.17E-06		1.764E-02	264.60
20000	3.369E-07	0.999	3.37E-07	1	6.738E-03	134.76



14-22

P14-11 cont'd



(2) Maximum mixedness : $F(t) = \int_0^t E(t) dt$

$$X_{i+1} = X_i + (\Delta\lambda) \left[\frac{X(\lambda_i)}{1 - F(\lambda_i)} X_i - k_c C_{A0} (1 - X_i)^2 \right]$$

When t is small, the plot E(t) vs t is very much a straight line. Therefore we can interpolate to obtain intermediate values of E(t).

t	E(t)	F(t)
0	3.25e-3	
5	3.187e-3	
10	3.124e-3	0.032
15	3.064e-3	
20	3.005e-3	0.062
25	2.945e-3	
30	2.889e-3	0.091
35	2.832e-3	
40	2.776e-3	0.118
45	2.766e-3	
50	2.673e-3	0.143
55	2.622e-3	
60	2.570e-3	0.169
65	2.519e-3	
70	2.468e-3	0.194

14-23

P14-11 cont'd

λ	X
70	0
60	0.5
50	0.61
40	0.67
30	0.70
20	0.72
10	0.74
0	0.75

$$X = 0.75$$

Part (b)

Tanks in series : $n = \frac{\tau^2}{\sigma^2}$ $\tau = \frac{V}{v_0} = \frac{1000}{1} = 1000s$

$$\int_0^{\infty} t E(t) dt = 995$$

$$\int_0^{\infty} t^2 E(t) dt = 5.656e6$$

$$n = \frac{\tau^2}{\sigma^2} = \frac{(10^3)^2}{4.666e6} = 0.214$$

$$X = 1 - \frac{1}{(1 + \tau k)^n} = 1 - \frac{1}{\left(1 + \frac{\tau}{n} k\right)^n} = 1 - \frac{1}{\left(1 + \frac{1000}{0.214} \cdot 0.005\right)^{0.214}}$$

$$X = 0.495$$

Part (c)

Two CSTR's in parallel

Assume the two CSTR's are equal in volume

$$V = \frac{F_{A0}X}{-r_A} = \frac{v_0X}{k \cdot C_{A0}(1-X)^2}$$

14-24

P14-11 cont'd

with $V_1 = V_2 = \frac{V}{2}$ and $v_{01} = v_{02} = \frac{v_0}{2}$, the conversion X , will be the same as for one CSTR with volume V and flowrate v_0 .

$$V = \frac{v_0 X}{k \cdot C_{A0}(1-X)^2}$$

$$\frac{X}{(1-X)^2} = \frac{V k C_{A0}}{v_0} = \frac{1000)(0.005 \cdot 10}{1} = 50$$

gives $X = 0.868$ but iteration (or could solve the quadratic)

Part (d)

For a CSTR
$$V = \frac{v_0 X}{k \cdot C_{A0}(1-X)^2}$$

From Part (c) $X = 0.868$

For a PFR :
$$X = \frac{k C_{A0} \tau}{1 + k C_{A0} \tau}$$
 For $t = \tau$, $X_{\text{CSTR}} = 0.868$, $X_{\text{PFR}} = 0.980$

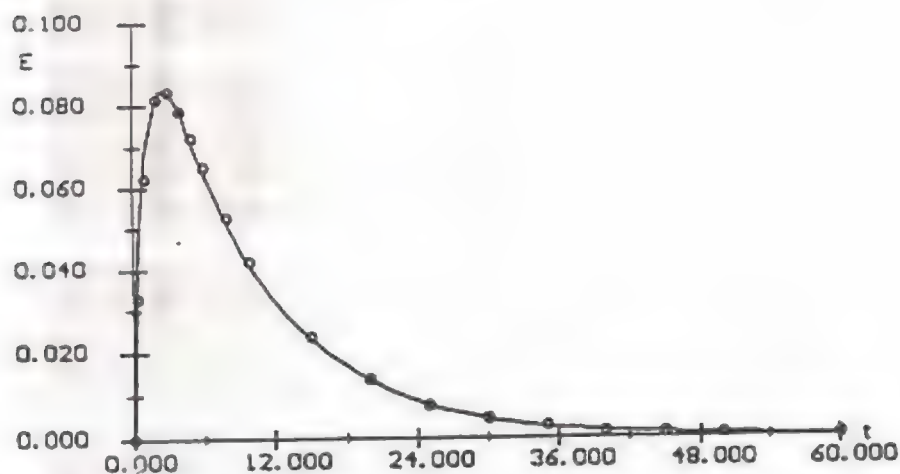
Summary :

	Conversion, X
Maximum segregation	0.868
Minimum segregation	0.75
Tanks in series	0.5
2 CSTR's in parallel	0.868
Single CSTR	0.868
Single PFR	0.980

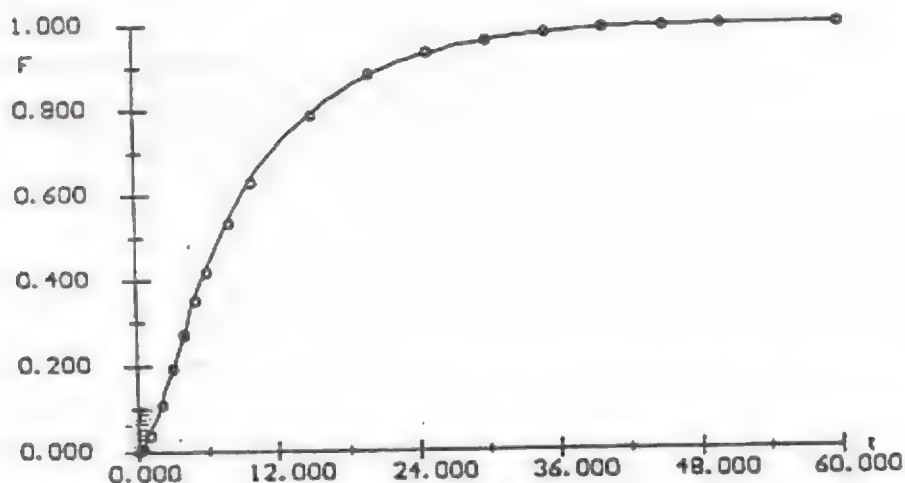
14-25

(a) Plot $E(t)$ vs t

P14-13



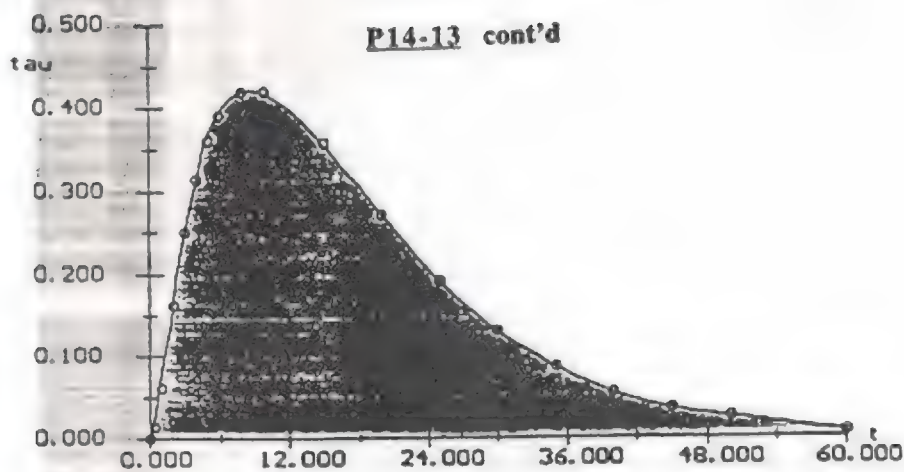
(b) Plot $F(t)$ vs t



(c) Find t_m

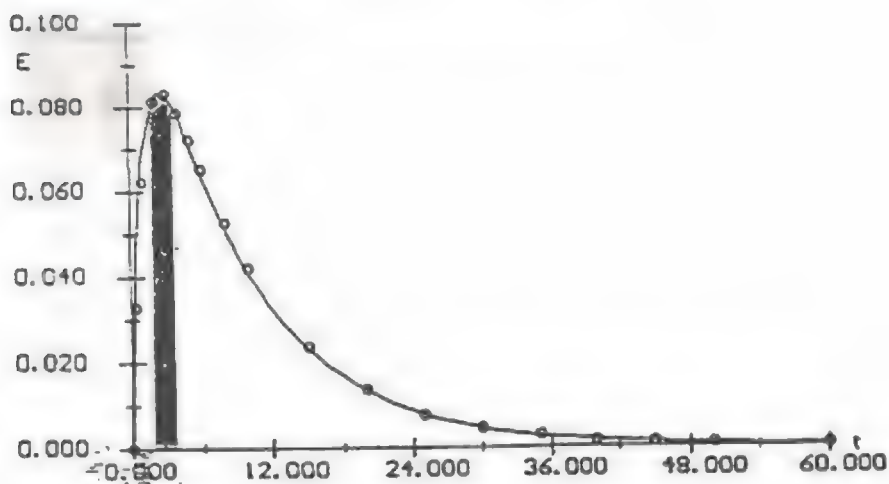
14-26

P14-13 cont'd



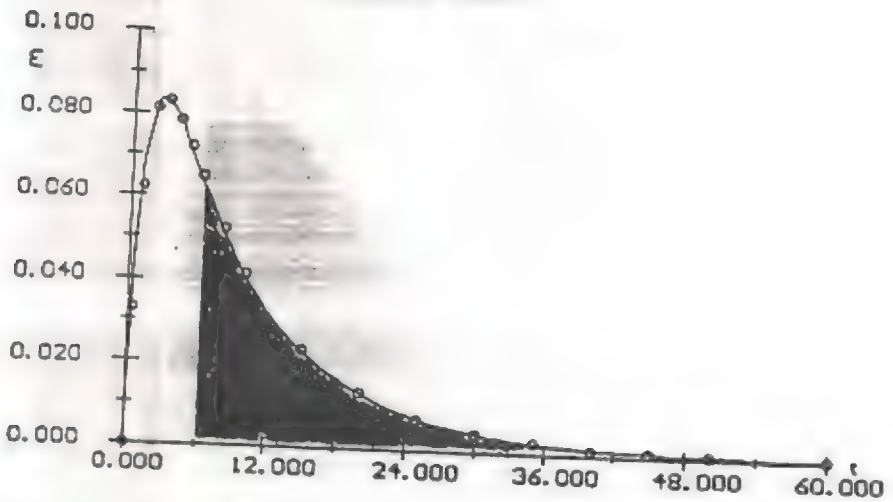
$$t_m = \tau = \int_0^{\infty} tE(t)dt = 9.95$$

(d) Fraction that spends between 2 and 4 minutes



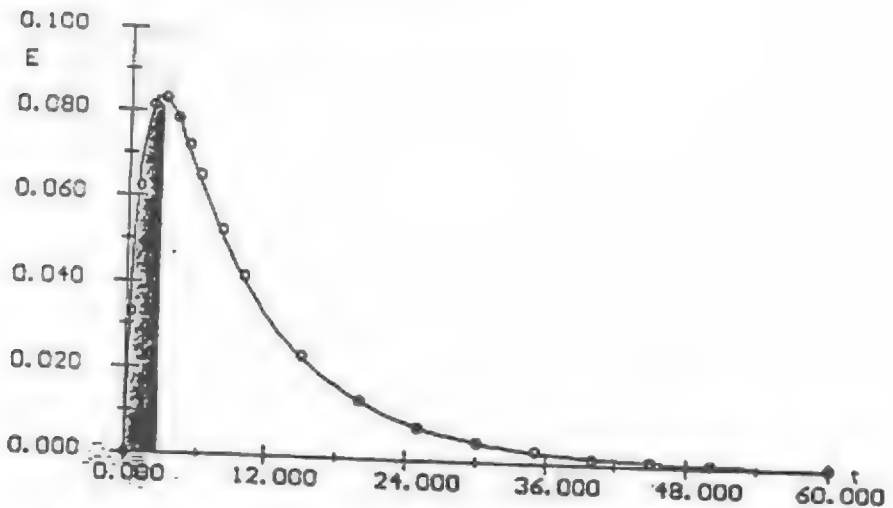
$$Fract = \int_2^4 tE(t)dt = 16.3\%$$

(e) Fraction that spends longer than 6 minutes



$$Fract = \int_6^{\infty} tE(t)dt = 58.3\%$$

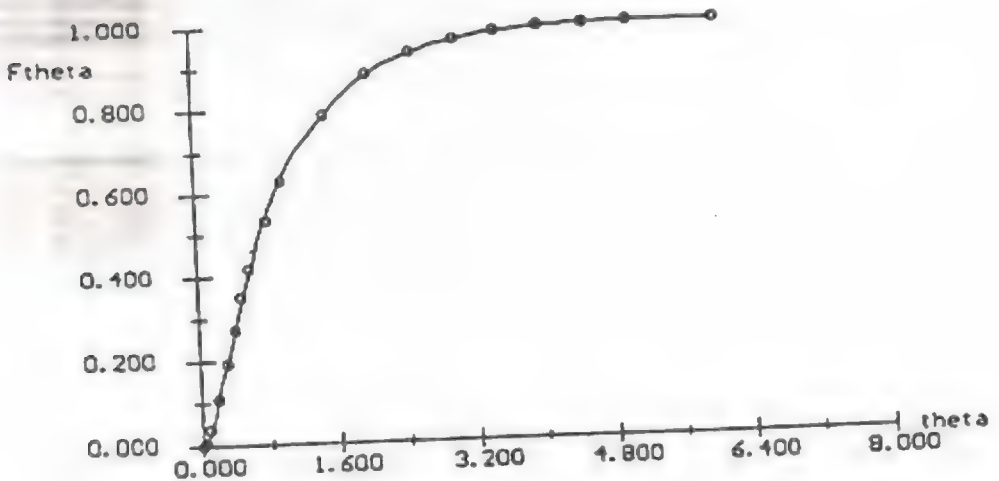
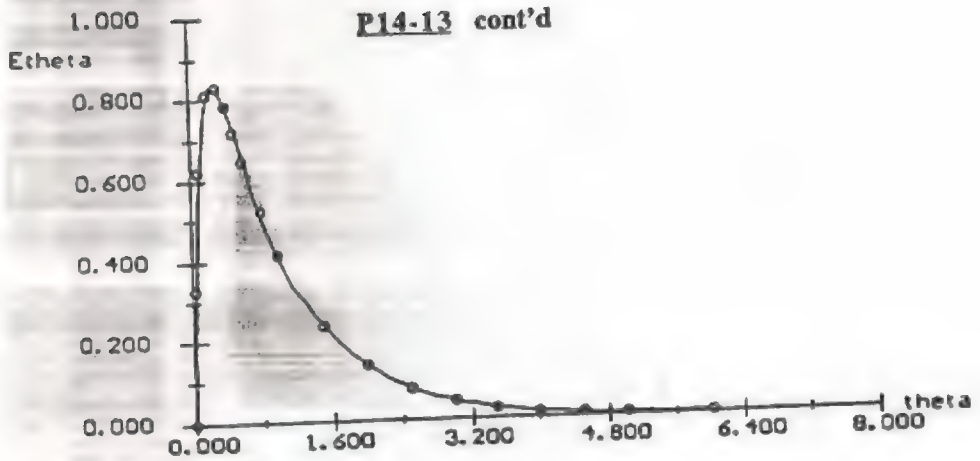
(f) Fraction that spends less than 3 minutes



$$Fract = \int_0^3 tE(t)dt = 19.4\%$$

(g) $E(\Theta)$ and $F(\Theta)$ vs. Θ

P14-13 cont'd



(h) Reactor Volume:

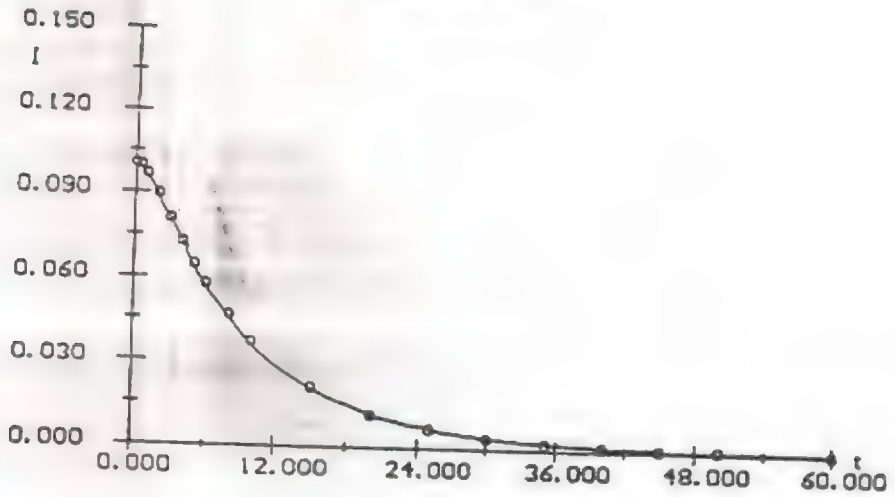
$$V = v\tau$$

$$V = \left(10 \frac{\text{dm}^3}{\text{min}} \right) (9.95 \text{ min}) = 99.5 \text{ dm}^3$$

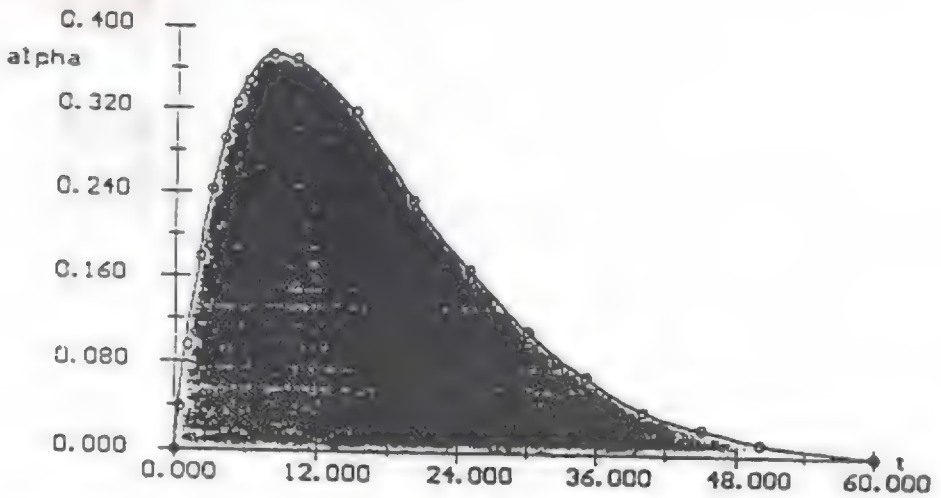
(i) Plot $I(t)$ vs. t

14-29

P14-13 cont'd



(j) Find α_m



$$\alpha_m = \int_0^{\infty} I(t) dt = 8.63$$

(k) Plot $\Delta(t)$ vs. t

14.30

$$V = \frac{F_{A0}X}{-r_A}$$

$$-r_A = kC_A^2$$

$$C_A = C_{A0}(1-X)$$

$$V = \frac{X}{\frac{kC_{A0}(1-X)^2}{V}}$$

$$\frac{X}{(1-X)^2} = 1$$

$$X = 38.2\%$$

(p) Find the conversion for a segregation model.

$$-\frac{dN_A}{dt} = -r_A V$$

$$-r_A = kC_A^2$$

$$C_A = C_{A0}(1-X)$$

$$\frac{dX}{dt} = \frac{-r_A V}{N_{A0}}$$

$$\frac{dX}{dt} = kC_{A0}(1-X)^2$$

$$\int_0^X \frac{dX}{(1-X)^2} = \int_0^t 0.1 dt$$

$$\frac{1}{1-X} - 1 = 0.1t$$

$$X = 1 - \frac{1}{1+0.1t}$$

$$\bar{X} = \int_{\frac{t}{2}}^{\infty} X(t) E(t) dt = 42.3\%$$

P14-13 cont'd

- (q) Find the conversion for a maximum mixedness model.

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{A0}} + \frac{E(\lambda)}{1-F(\lambda)}(X)$$

$$-r_A = kC_A^2$$

$$C_A = C_{A0}(1-X)$$

Integrate from $\lambda = \infty \rightarrow 0$ using POLYMATH

Equations

Maximum Mixedness Model

Initial values

$$d(x)/d(z) = -(r_A/C_{A0} + EF \cdot x)$$

$$d(F)/d(z) = -E$$

$$C_{A0} = 1$$

$$k = 1$$

$$\lambda_m = 60 - z$$

$$C_A = C_{A0}(1-x)$$

$$E1 = -.0011721 \times \lambda_m^4 + .0113999 \times \lambda_m^3 - .0476813 \times \lambda_m^2 + .0999015 \times \lambda_m$$

$$E2 = 2.79737 \times 10^{-8} \times \lambda_m^4 - 4.94398 \times 10^{-6} \times \lambda_m^3 + .000326287 \times \lambda_m^2 - .00968055 \times \lambda_m + .111693$$

$$r_A = -k \times C_A^2$$

$$E = \text{if } (\lambda_m < 3) \text{ then } (E1) \text{ else } (E2)$$

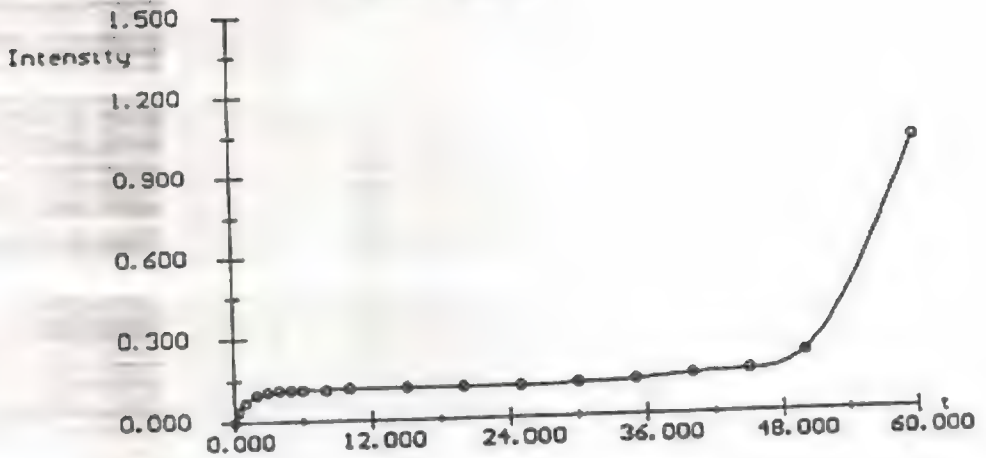
$$EF = E / (1-F)$$

$$z_0 = 0, \quad z_f = 60$$

$$X = 40.4\%$$

14-34

P14-13 cont'd



- (1) Find the mean catalytic activity with a second order decay law

$$-\frac{da}{dt} = k_p a^2$$

where

$$k_p = 0.15^{-1}$$

$$-\int_1^a \frac{da}{a^2} = \int_0^t 6 \text{ min}^{-1} dt$$

$$-\frac{1}{a} \Big|_1^a = 6t \Big|_0^t$$

$$\frac{1}{a} - 1 = 6t$$

$$a = \frac{1}{6t + 1}$$

$$\bar{a} = \int_0^1 a I(\alpha) d\alpha$$

$$\bar{a} = 0.0725$$

P14-13 cont'd

- (m) Find the conversion for a PFR with a second order reaction where $kC_{A0} = 0.1 \text{ min}^{-1}$

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

$$-r_A = kC_A^2$$

$$C_A = C_{A0}(1-X)$$

$$\frac{dX}{dV} = \frac{kC_{A0}(1-X)^2}{v} = \frac{(0.1)(1-X)^2}{10}$$

$$\int_0^X \frac{dX}{(1-X)^2} = \int_0^{99.5} 0.01 dV$$

$$\left. \frac{1}{1-X} \right|_0^X = 0.995$$

$$X = 50\%$$

- (n) Find the conversion for a laminar flow reactor.

$$E(t) = 0 \quad t < \frac{\tau}{2}$$

$$E(t) = \frac{\tau^2}{2t^3} \quad t \geq \frac{\tau}{2}$$

$$t_m = \int_{\frac{\tau}{2}}^{\tau} tE(t)dt = \tau$$

With a second order reaction occurring,

$$X = 1 - \frac{1}{1+0.1t}$$

The mean conversion for the system is

$$\bar{X} = \int_{\frac{\tau}{2}}^{\tau} X(t)E(t)dt = 44.3\%$$

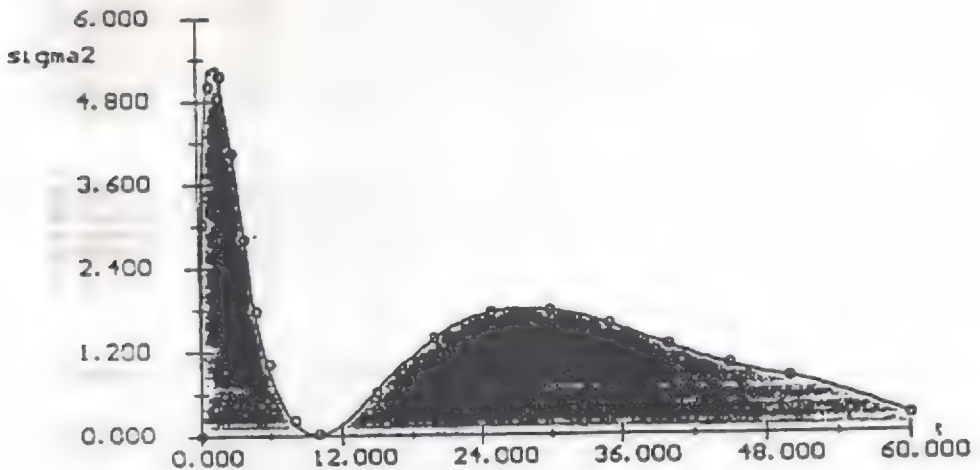
- (o) Find the conversion for a CSTR

14-32

P14-13 cont'd

- (r) How many tanks are needed to represent this reactor in a tanks-in-series model? Find the conversion for a first order reaction where

$$k = 0.1 \text{ min}^{-1}$$



$$\sigma^2 = \int_0^{\infty} E(t)(t - t_m)^2 dt = 75.2$$

$$n = \frac{\tau^2}{\sigma^2} = 1.32$$

$$X = 1 - \frac{1}{(1 + \tau_i k)^n}$$

$$\tau_i = \frac{V}{v_0 n}$$

$$X = 52.4\%$$

- (s) Using the dispersion model, find the Peclet number. What is the conversion of a first order reaction where

$$k = 0.1 \text{ min}^{-1}$$

For a Closed-Closed Vessel:

14-35

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2} (1 - e^{-Pe_r})$$

$$Pe_r = 0.8875$$

$$X = 1 - \frac{4q \exp\left[\frac{Pe_r}{2}\right]}{(1+q)^2 \exp\left[\frac{Pe_r q}{2}\right] - (1-q)^2 \exp\left[\frac{-Pe_r q}{2}\right]}$$

$$Da = \tau k = 0.995$$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}} = 2.34$$

$$X = 52.75\%$$

For an Open-Open Vessel:

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2}$$

$$Pe_r = 4.861$$

$$Da = \tau k = 0.995$$

$$q = \sqrt{1 + \frac{4Da}{Pe_r}} = 1.35$$

Note: Conversion cannot be calculated using the previously found equation because the boundary conditions are not the same.

(i) For second order rxn:

$$Da = kC_{A0}\tau = 0.995$$

For closed system:

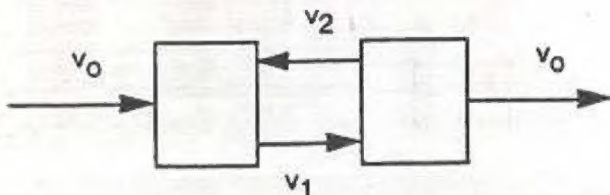
$$q = \sqrt{1 + \frac{4Da}{Pe_r}}, \quad Pe_r = 0.8875$$

$$= 2.34$$

$$x = 52.8\%$$

P14-13 cont'd

(u) It is suspected that the reactor might be behaving as shown below. What is the "backflow" from the second to the first vessel as a multiple of v_0 ?



$$V \frac{dC_1}{dt} = (v_0 C_0 + v_2 C_2) - v_1 C_1$$

$$V \frac{dC_2}{dt} = v_1 C_1 - (v_0 C_2 + v_2 C_2)$$

$$V \frac{dC_1}{dt} = \beta v_0 C_2 - (1 + \beta) v_0 C_1$$

$$V \frac{dC_2}{dt} = (1 + \beta) v_0 C_1 - (v_0 C_2 + \beta v_0 C_2)$$

$$V \frac{d^2 C_1}{dt^2} = (1 + \beta) v_0 \left(\frac{dC_1}{dt} - \frac{dC_2}{dt} \right)$$

$$V \frac{d^2 C_2}{dt^2} = (1 + \beta) v_0 \left(\frac{\beta v_0 C_2 - (1 + \beta) v_0 C_1}{V} - \frac{dC_2}{dt} \right)$$

$$V \frac{d^2 C_2}{dt^2} = (1 + \beta) v_0 \left(\frac{\beta v_0 C_2 - (1 + \beta) v_0 \left(\frac{V_2 \frac{dC_2}{dt}}{v_0 (1 + \beta)} + C_2 \right)}{V} - \frac{dC_2}{dt} \right)$$

$$V \frac{d^2 C_2}{dt^2} + 2(1 + \beta) v_0 \frac{dC_2}{dt} + \frac{(1 + \beta) v_0^2}{V} C_2 = 0$$

$$m_1, m_2 = \frac{-2(1 + \beta) v_0 \pm \sqrt{(2(1 + \beta) v_0)^2 - 4V \left(\frac{(1 + \beta) v_0^2}{V} \right)}}{2V}$$

$$m_1, m_2 = \frac{-(1 + \beta) v_0 \pm v_0 \sqrt{\beta^2 + \beta}}{V}$$

We will define m_1 as:

14-37

P14-13 cont'd

$$m_1 = \frac{-(1+\beta)v_0 + v_0\sqrt{\beta^2 + \beta}}{V}$$

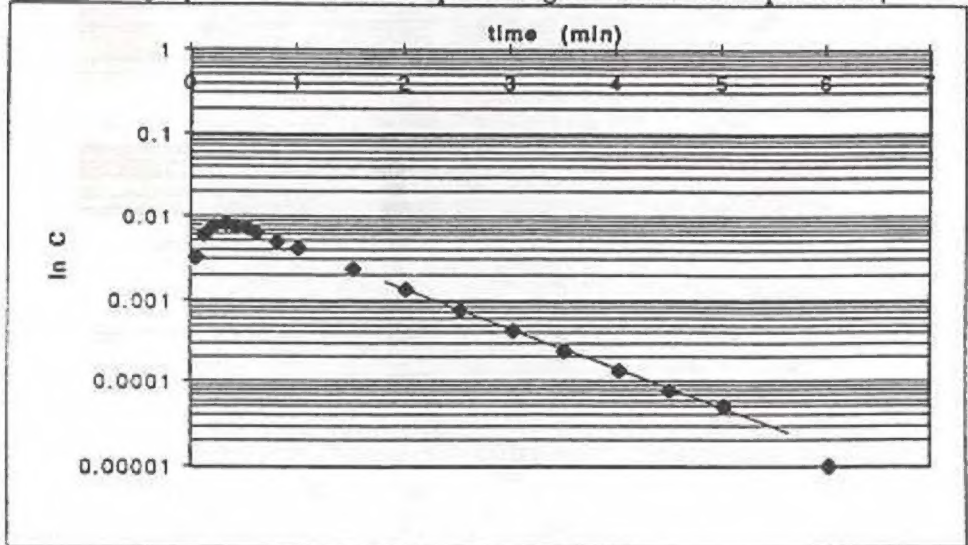
C_2 is defined as:

$$C_2 = Ae^{m_1 t} + Be^{m_2 t}$$

Because m_1 is smaller in magnitude than m_2 , we know that m_1 will dominate at higher times. Therefore, at large time,

$$C_2 = Ae^{m_1 t}$$

When we graph $\ln C$ vs. t , the slope at large time will be equal to m_1 .



The slope was found to be 0.1173.

Solving, we find that $\beta \approx 1.0$.

So backflow = v_0 .

(v)

$$\text{Reactor 1: } C_{A0}v_0 + C_{A2}v_0 - 2C_{A1}v_0 - kC_{A1}^2V = 0$$

$$\text{Reactor 2: } 2C_{A1}v_0 - C_{A2}v_0 - C_{A2}^2V - kC_{A2}^2V = 0$$

Solving for C_{A1} in Reactor 2 yields:

$$2C_{A1}v_0 = 2C_{A2}v_0 + kC_{A2}^2V$$

P14-13 cont'd

Plugging into equation 1 and simplifying $\left(\tau = \frac{V}{v_0} = 0.995 * 5, C_{A0} = 1 \right)$

We get

$$1 + C_{A2} - 2C_{A2} - 0.4975 \left[C_{A2}^2 + \left(\frac{2C_{A2} + 0.4975C_{A2}^2}{2} \right) \right] = 0$$

Solving by trial and error:

$$C_{A2} = 0.545$$

$$X = 0.455$$

w)

Reactor Model	Conversion (%)
PFR	50.0
Laminar Flow	44.3
CSTR	38.2
Segregation	42.3
Maximum Mixedness	40.4
Tanks in Series	52.4
Dispersion (Closed-Closed)	52.8
Dispersion (Open-Open) "Backflow"	45.5